Some Gallium Phosphate Frameworks Related to the Aluminium Phosphate Molecular Sieves: *X*-Ray Structural Characterization of $\{(\text{Pr}^i\text{NH}_3)[\text{Ga}_4(\text{PO}_4)_4\cdot\text{OH}]\}\cdot\text{H}_2\text{O}$†

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Several galliophosphate frameworks have been synthesised; some of the structures are related to the AlPO_4-family of molecular sieves and the structure of $\{(\text{Pr}^i\text{NH}_3)[\text{Ga}_4(\text{PO}_4)_4\cdot\text{OH}]\}\cdot\text{H}_2\text{O}$ has been shown to be related to AlPO_4-12,-15, and -21.†

The synthesis of aluminophosphate frameworks,[1,2] some of which have potential as absorbants and as supports for catalytically active metals,[1] has suggested framework structures with other compositions may be possible complements to the range of zeolite (aluminosilicate) molecular sieves.[3,4] Galliophosphates synthesised recently are briefly reported here.

Their synthesis is associated with a specific structure directing agent added to a gel of composition close to $1.0\ \text{R}\cdot\text{Ga}_2\text{O}_3\cdot\text{P}_2\text{O}_5\cdot40\text{H}_2\text{O}$; here R is the template, usually an organic amine. These gels are treated hydrothermally at between 150 and 200 °C in evacuated thick walled Pyrex tubes. If the director is excluded no open frameworks are formed. Details of the synthetic conditions used and the crystallographic properties of some of the compounds produced are summarized in Table 1. A comparison of characteristic *X*-ray powder diffraction patterns[1] suggested some of these compounds are analogues of the AlPO_4-frameworks. Indeed structural determinations, using single crystal *X*-ray techniques, confirm phases 2, 4, and 5 (Table 1) are analogues of AlPO_4-12, -21, and -25, respectively.[4—7] Phase number 3 (Table 1) has composition $\text{Ga}_4(\text{PO}_4)_4\cdot2\text{H}_2\text{O}\cdot\text{NC}_3\text{H}_9$ and represents a new structure type with a powder pattern closely resembling that of AlPO_4-14.[1]† Although a full structural analysis of AlPO_4-14 is required to establish properly the relationship between the two compounds, phase 3 will hereafter be referred to as GaPO_4-14.

The framework‡ consists of the units shown in Figure 2,

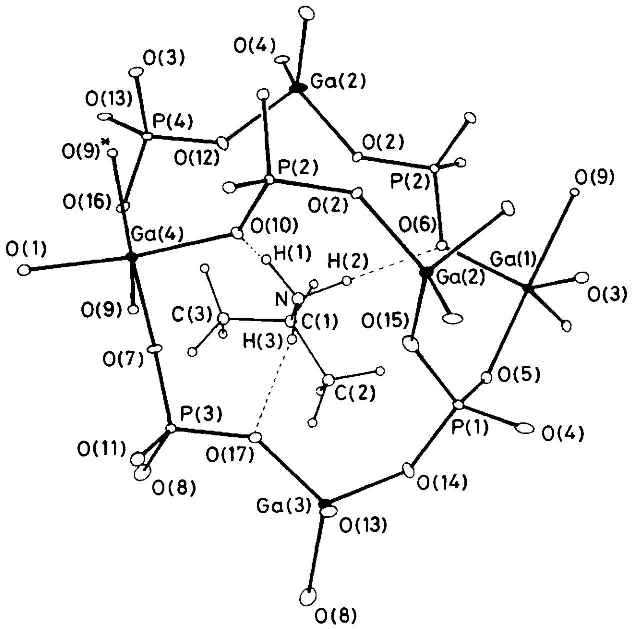

Figure 1. ORTEP drawing showing the environment about the iso-propylamine molecule in GaPO_4-14. The full asymmetric unit is shown. Selected bond lengths and average bond lengths are P–O 1.53, Ga(1)–O 1.92, Ga(2)–O 1.82, Ga(3)–O 1.81, Ga(4)–O 1.97, Ga(1)–O(9) 2.138(3), Ga(4)–O(9) 2.053(3), Ga(4)–O(9*) 2.084(3) Å. O(9) represents the position of an hydroxy group whose removal allows the framework to consist of alternating GaO_4- and PO_4-polyhedra (see Figure 2 and text).

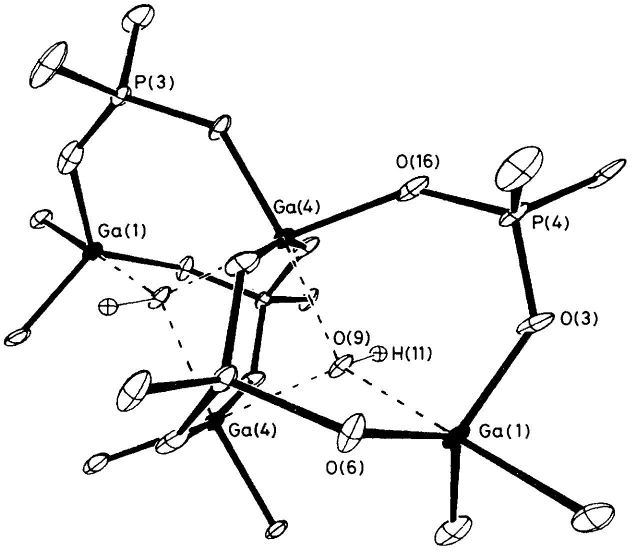

Figure 2. ORTEP drawing of the Ga_4-cluster found in GaPO_4-14. Thin lines represent bonds between Ga and hydroxy groups whose removal produces a structure containing alternating four-co-ordinated gallium- and phosphorus centred polyhedra.

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† The nomenclature used to distinguish frameworks in this communication follows that established by workers at Union Carbide (reference 1), who named new aluminophosphate phases AlPO_4-*n*, where AlPO_4 designates the approximate framework composition and *n* denotes a unique structure type.

‡ *Crystal data* for GaPO_4-14, triclinic, space group $P\bar{1}$, $a = 9.601(2)$, $b = 9.757(2)$, $c = 10.701(2)$ Å, $\alpha = 74.20(1)°$, $\beta = 75.01(1)$, $\gamma = 88.48(1)°$, $U = 930.7$ Å^3, $D_c = 2.69$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 60.8$ cm^{-1}, $Z = 2$, $\lambda = 0.7107$ Å, crystal dimensions $0.15 \times 0.13 \times 0.03$ mm, $R = 0.034$, $R_w = 0.039$ for 3661 reflections with $I > \sigma(I)$, collected at 23 °C on a PICKER-FACSI diffractometer; data corrected for absorption effects, structure solved by direct methods and refined using SHELX-76;[8] hydrogen atoms attached to nitrogen, the pivotal carbon atom, and four of six remaining hydrogens were located by difference Fourier synthesis; the remainder were calculated from refined carbon positions assuming ideal C–H distances and angles. 1.09 Molecules of water located within the pores of the structure do not play any obvious structural role. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Synthetic conditions and crystallographic data for selected $GaPO_4$ compounds.

Phase[a]	Structure[b] type	Synthesis[c]	Typical template	Space group or crystal class	Cell parameters[d] *a*	*b*	*c*	α	β	γ
1	—	200/63	Ethylenediamine	$P2_1/c$	4.49	5.98	18.53	90.0	94.5	90.0
2	$AlPO_4$-12	200/63	Ethylenediamine	$P2_1/c$	14.656(2)	9.625(1)	9.672(1)	90.0	97.89(1)	90.0
3	$AlPO_4$-14	200/142	Iso-propylamine	$P\bar{1}$	9.601(2)	9.757(2)	10.701(2)	74.20(1)	75.01(1)	88.48(1)
4	$AlPO_4$-21[e]	200/86	Pyrrolidine	$P2_1/n$	8.700(1)	18.146(2)	9.087(1)	90.0	107.3(1)	90.0
5	$AlPO_4$-25[f]	650/48	—	Orthorhombic	8.400	18.49	15.03	90.0	90.0	90.0
6	—	150/312	NEt_4OH[g]	Hexagonal	12.63	12.63	17.06	90.0	90.0	120.0

[a] Structures distinguished on the basis of their characteristic *X*-ray powder diagrams using a Guinier camera. [b] *X*-Ray powder and single crystal techniques were used to suggest those structures analogous to the $AlPO_4$-frameworks (see reference 1). [c] The temperature (°C) and time (h) of reaction. [d] Cell parameters determined from single crystal diffractometry (12 fully centred reflections on a PICKER FACSI diffractometer, estimated standard deviations quoted in brackets) or from Weisenberg and precession photographs (no e.s.d.'s quoted). [e] Also synthesised using iso-propylamine. [f] Calcined phase 4. [g] This structure-type also synthesised using quinuclidine.

cross-linked *via* GaO_4- and PO_4-tetrahedra, to produce pores which accommodate the iso-propylamine template. Hydrogen atoms have been located in this analysis (Figure 1) and indicate that the template is charged, $[NC_3H_{10}]^+$ resulting in a structural formula, $\{(Pr^iNH_3)\cdot[Ga_4(PO_4)_4\cdot OH]\}\cdot H_2O$. Iso-propylamine is hydrogen bonded (Figure 1) to the framework *via* N–H(1) · · · O(10) [H(1) · · · O(10), 2.32 Å], N–H(2) · · · O(6) [H(2) · · · O(6), 1.95 Å], N–H(3) · · · O(17) [H(3) · · · O(17), 2.09 Å].

The structure‡ (Figures 1 and 2) is related to those of $AlPO_4$-12 -15, and -21.[4—7] All of these compounds contain phosphorus in four-co-ordination with oxygen (tetrahedra) along with 4-,5-, and 6-co-ordinate Al-centred polyhedra. In $GaPO_4$-14, the major building unit consists of edge and corner shared 5- and 6-co-ordinate gallium. Figure 2 shows this unit in $GaPO_4$-14, with edge-shared octahedra connected *via* corners with two trigonal bipyramids of $GaO_4(OH)$. The oxygen atom [O(9)], co-ordinating three gallium atoms, is in fact an hydroxy group similar to that found in $AlPO_4$-15.[9] The grouping (Figure 2) is then intermediate between the all-octahedral co-ordination found for aluminium in $AlPO_4$-15[9] and the all-trigonal bipyramidal configuration found for gallium in $GaPO_4$-12.[10]

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