Hydrothermal Synthesis and Crystal Structure of the Microporous Gallophosphate $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot4H_2O\cdot0.64PrOH$ with an Octahedral–Tetrahedral Framework†

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The new microporous gallophosphate, $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot4H_2O\cdot0.64PrOH$, has been synthesised and structurally characterised; it has a framework isostructural with that of $[NH_4][Al_2(OH)(HPO_4)_2]\cdot2H_2O$. The gallophosphate consists of gallium-centred octahedra (GaO_6) and phosphorus-centred tetrahedra (PO_4) which together serve as basic building units to form a three-dimensional framework structure. The gallophosphate crystallises in monoclinic symmetry with space group $P2_1/n$, $a = 9.6814(0)$, $b = 9.6568(0)$, $c = 9.7618(0)$ Å and $\beta = 102.90(5)°$. The structure possesses three-dimensional channels with eight-ring windows running along the [100], [010] and [001] axes in which organic template molecules and inorganic NH_4^+ cations in pairs are located.

Recently, the known range of zeolite structures has been increased substantially by the discovery that mixed TO_3, TO_4, TO_5 and TO_6 basic building blocks (where T represents a framework element) can be incorporated into the structures of non-conventional crystalline microporous solids. For instance, some three-dimensionally ordered, aluminophosphates have been described.[1] Following upon Parise's[2] reported structure of a microporous gallophosphate, in which a mixture of four-, five- and six-co-ordinated Ga atoms were found a search for mixed SnO_6–SiO_4 and MoO_6–PO_4 microporous framework structures was conducted at EXXON.[3] Systematic syntheses of R–Ga_2O_3–P_2O_5–H_2O,[4–6] R–M_2O–Al_2O_3–B_2O_3–H_2O[7] and R–M_2O–Al_2O_3–TiO_2–H_2O systems,[8] where R is a templating agent and M is an alkali or alkaline-earth metal, have been conducted in our laboratory in recent years. Twelve types of R–Ga_2O_3–P_2O_5–H_2O systems of differing composition were identified to give rise to three-dimensional framework structures, among which some are the structural analogues of known aluminophosphate molecular sieves.[1,9] Others have been shown to have novel phases from characterization by X-ray diffraction and from their adsorption properties. Compared to the crystalline microporous aluminophosphates developed by Wilson *et al.*[1] the resulting gallophosphates possess more complicated framework structures, due to the range of co-ordination environments around the gallium atom; by exploiting this flexibility one may further explore novel microporous framework structures.

Here we report the detailed synthesis and crystal structure of the microporous gallophosphate $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot4H_2O\cdot0.64PrOH$.

Experimental

The compound $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot4H_2O\cdot0.64$ was synthesised by a hydrothermal reaction. An aqueous mixture of hydrated Ga(O)OH, prepared from the calcination of $Ga(OH)_3$ hydrogel, 85% phosphoric acid, and propylamine ($PrNH_2$) with an initial gel composition $2.2PrNH_2 : 1.0Ga_2O_3 : 1.2P_2O_5 : 50H_2O$ was sealed in a Teflon-lined autoclave and heated at 200 °C for 3 d under autogenous pressure. The crystalline product, which appeared to be uniform and polyhedral-shaped, was filtered off, washed with distilled water and dried at ambient temperature.

A single crystal with approximate dimensions of 0.3 × 0.2 × 0.2 mm was selected for intensity collection on a Nicolet R3 four-circle diffractometer using the ω-scan technique with variable scan speed, 4.0–29.3° min^{-1}, in the range $3 < 2\theta < 67°$. The total number of reflections measured was 3340, of which 2946 with $F > 3\sigma(F)$ were considered as unique observed. All data were corrected by the L_P factor and for absorption. The structure was solved by direct methods and refined by block-matrix least-squares. All computations were carried out on an Eclipse S/250 computer using the SHELXTL[10] program. All hydrogen atoms except those of PrOH were revealed from a Fourier-difference map.

Crystal and experimental data for the structural characterisation are listed in Table 1.

Results and Discussion

The composition analysis of the sample corresponds to the unit cell being $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot4H_2O\cdot0.64PrOH$. Atomic parameters, selected bond lengths and angles are given in Tables 2–4.

The structure consists of gallium-centred octahedra and phosphorus-centred tetrahedra. The co-ordination environment of gallium and phosphorus atoms in the asymmetric unit is shown in Fig. 1. Each phosphorus atom is tetrahedrally co-ordinated and shares an oxygen atom with an adjacent gallium atom. Both gallium atoms are co-ordinated by six oxygen atoms which form a slightly distorted octahedron. Eight of the eleven oxygen atoms are bonded to one phosphorus atom and one gallium atom. The atom O(10) (from a water molecule) is only bonded to one gallium atom [Ga(1)], whereas O(11), also from a water molecule of crystallisation, is not bonded to Ga or P. Finally, O(1), from a hydroxyl group, is co-ordinated to three gallium atoms Ga(1), Ga(2) and Ga(2a) to form a disordered tetrahedron.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Crystallographic data for $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot 4H_2O\cdot 0.64PrOH$

Formula weight	1636.28
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.6814(0)
b/Å	9.6568(0)
c/Å	9.7618(0)
β/°	102.90(5)
U/Å^3	889.59
Z	4
Crystal size (mm)	0.3 × 0.2 × 0.2
D/g cm^{-3}	2.86
Radiation	Mo-Kα (λ = 0.710 69 Å)
μ(Mo-Kα)/cm^{-1}	67.45
Reflections measured	3340
Observed unique reflections [$F > 3\sigma(F)$]	2946
R	0.0361
R'	0.0342

Table 2 Fractional atomic coordinates (×10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Ga(1)	−1 018.5(0.4)	12 678.1(0.4)	6 844.2(0.4)
Ga(2)	1 132.6(0.4)	9 578.6(0.4)	6 293.7(0.4)
P(1)	2 072.3(0.8)	11 854.8(0.8)	8 670.4(0.8)
P(2)	−2 027.0(0.8)	9 667.0(0.8)	6 496.0(0.8)
O(1)	−2(2)	8 588(2)	4 422(2)
O(2)	2 127(2)	8 895(2)	2 836(2)
O(3)	2 383(2)	10 169(2)	5 128(2)
O(4)	1 876(2)	6 290(2)	1 861(2)
O(5)	2 609(2)	11 696(2)	10 248(2)
O(6)	2 048(2)	7 885(2)	6 964(2)
O(7)	−517(2)	7 711(2)	1 594(2)
O(8)	−512(2)	9 095(2)	7 006(2)
O(9)	2 202(2)	10 424(2)	7 982(2)
O(10)	−42(2)	5 583(3)	3 490(3)
O(11)	1 815(3)	3 536(3)	4 633(3)
N	4 877(3)	18 886(4)	6 030(3)

Table 3 Selected bond lengths (Å) with e.s.d.s in parentheses

Ga(1)–O(1)	2.131(2)	P(1)–O(9a)	1.554(3)
Ga(1)–O(2)	1.925(2)	P(2)–O(2)	1.546(2)
Ga(1)–O(4)	1.936(2)	P(2)–O(3)	1.553(2)
Ga(1)–O(5)	1.907(2)	P(2)–O(8)	1.542(2)
Ga(1)–O(7)	1.914(2)	P(2)–O(4a)	1.510(3)
Ga(1)–O(10)	2.031(3)	O(1)–H(1a)	1.003(11)
Ga(2)–O(1)	2.136(2)	O(10)–H(1b)	0.859(10)
Ga(2)–O(3)	1.924(2)	O(10)–H(2b)	0.888(10)
Ga(2)–O(6)	1.905(2)	O(11)–H(1c)	0.849(12)
Ga(2)–O(9)	1.921(2)	O(11)–H(2c)	0.802(10)
Ga(2)–O(1a)	2.117(2)	N–H(1d)	0.940(11)
Ga(2)–O(8a)	1.932(2)	N–H(2d)	0.860(11)
P(1)–O(7)	1.527(3)	N–H(3d)	0.877(11)
P(1)–O(5a)	1.519(2)	N–H(4d)	0.904(9)
P(1)–O(6a)	1.528(3)		

Table 4 Selected bond angles (°) with e.s.d.s in parentheses

O(1)–Ga(1)–O(2)	89.4(1)	O(2)–P(2)–O(3)	108.5(1)
O(1)–Ga(1)–O(4)	174.6(1)	O(2)–P(2)–O(8)	109.3(1)
O(1)–Ga(1)–O(5)	92.1(1)	O(2)–P(2)–O(4a)	109.7(1)
O(1)–Ga(1)–O(7)	88.3(1)	Ga(1)–O(1)–Ga(2)	124.1(1)
O(1)–Ga(1)–O(10)	93.7(1)	Ga(1)–O(7)–P(1)	138.5(2)
O(1)–Ga(2)–O(3)	84.1(1)	Ga(2)–O(3)–P(2)	127.5(1)
O(1)–Ga(2)–O(6)	91.2(1)	O(10)–Ga(1)–H(1b)	130.0(7)
O(1)–Ga(2)–O(9)	178.1(1)	O(10)–Ga(1)–H(2b)	128.8(7)
O(1)–Ga(2)–O(1a)	87.9(1)	H(1c)–O(11)–H(2c)	97(1)
O(1)–Ga(2)–O(8a)	83.8(1)	H(1d)–N–H(2d)	96(1)
O(7)–P(1)–O(5a)	107.5(1)	H(1d)–N–H(3d)	102(1)
O(7)–P(1)–O(6a)	111.7(1)	H(1d)–N–H(4d)	109(1)
O(7)–P(1)–O(9a)	110.0(1)		

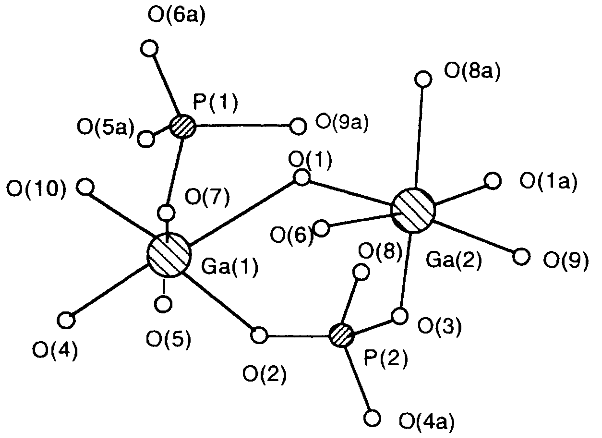

Fig. 1 The asymmetric unit of $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot 4H_2O\cdot 0.64PrOH$ showing the co-ordination of Ga and P atoms. Selected average bond lengths (Å) P–O 1.535, Ga(1)–O 1.974, Ga(1)–O(10) 2.032, Ga(1)–O(1) 2.131, Ga(2)–O 1.989, Ga(2)–O(1) 2.136 Å; O(10) from a water molecule, O(1) from a hydroxyl group

The three-dimensional framework structure of $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot 4H_2O\cdot 0.64PrOH$ in the [001] direction is shown in Fig. 2 and the double chains of gallium atoms formed within the framework by the trigonal gallium groups along the [001] direction are shown in Fig. 3. The structure is composed of an open gallophosphate framework with the inclusion of disordered PrOH molecules and NH_4^+ cations to balance the framework charge, and there are three-, four- and eight-membered rings composed of GaO_6 octahedra and PO_4 tetrahedra. The framework, as shown in Fig. 4 in the [110] direction, reveals the mixed GaO_6 octahedra and PO_4 tetrahedra, with three-dimensional channels along the [100], [010] and [001] directions, respectively, which result from cross packing of boat-shaped eight-membered rings.

One of the unique structural features is that all Ga atoms are six-co-ordinated by O atoms. This contrasts with other microporous gallophosphates in which Ga atoms have mixed four-, five- and six-co-ordination.[2,4,5] Also three gallium-centred octahedra are linked by one oxygen atom (OH) in a similar manner to $[NH_4][Al_2(OH)(HPO_4)_2]\cdot 2H_2O$, where one oxygen atom is co-ordinated to three aluminium atoms.[10]

The basic building blocks are TO_6 and TO_4 polyhedra; similar structures were found in Nasicon,[11] such as $Na[Zr_2P_3O_{12}]$, where mixed octahedral ZrO_6 and tetrahedral PO_4 serve as basic building blocks. Other examples of structures with related frameworks include potassium phosphoantimonate, $K_5[Sb_5P_2O_{20}]$[12] and the microporous germanates, $M_3H[Ge_7O_{16}]$, where M = alkali metal.[13–15] All these structures have mixed TO_6–TO_4 frameworks, in which some oxygen atoms have co-ordination numbers greater than 2, and have been found to be ionic conductors.

In the synthesis of $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot 4H_2O\cdot 0.64PrOH$ propylamine was intended to be the templating agent, but X-ray structure analysis shows that propyl alcohol molecules, coupled with NH_4^+ cations in pairs, reside in the channels. The propyl alcohol molecules, formed by hydrolysis of propylamine during the synthesis, are apparently distributed in a disordered manner in the channels. It seems that both inorganic NH_4^+ cations and organic alcohol molecules act as the templates to fill the channels and balance the charge of the framework. It is not certain whether hydrolysis occurs in the

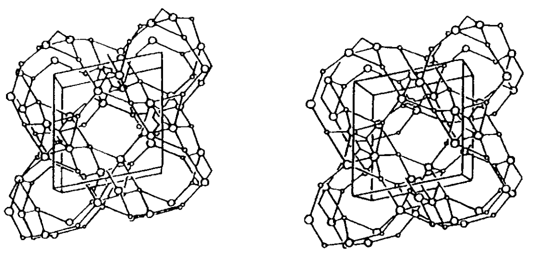

Fig. 2 The three-dimensional framework structure of $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot 4H_2O\cdot 0.64PrOH$ in the [001] direction: Ga atoms represented by large circles, P atoms by small circles (oxygen atoms not shown)

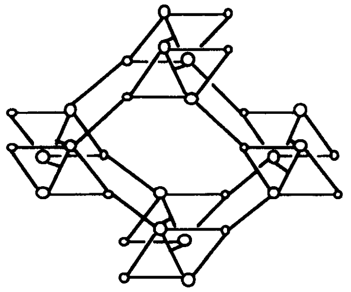

Fig. 3 Schematic plot of a sheet of $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot 4H_2O\cdot 0.64PrOH$ in the [001] direction showing the double chains formed by the connection of the trigonal gallium groups: Ga atoms represented by large circles, P atoms by small circles. The straight lines denote bonded bridging oxygen atoms

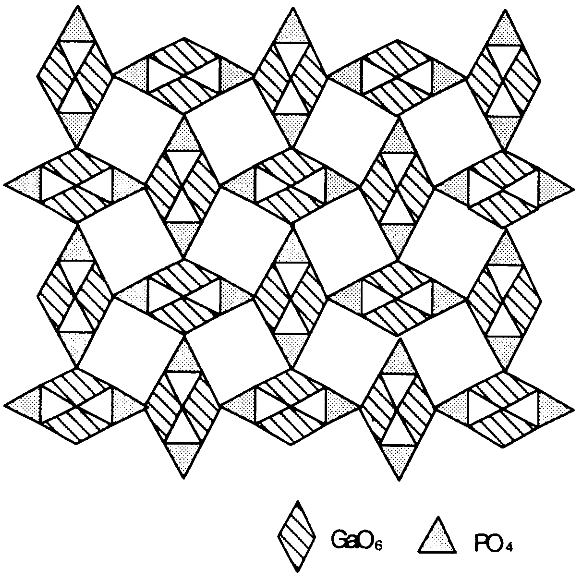

Fig. 4 Diagram of $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot 4H_2O\cdot 0.64PrOH$ showing the arrangement of mixed GaO_6 octahedra and PO_4 tetrahedra in the [110] direction

course of crystallisation or in the initial solution. What is interesting is the introduction of cations in the channels; if the structure is stable enough for organic species and NH_3 to be released upon heating, the proton form of the compound will be produced. The properties of the framework after loss of organics and NH_3 are being studied.

In summary, the microporous gallophosphate $[NH_4]_4[Ga_8P_8O_{32}(OH)_4(H_2O)_4]\cdot 4H_2O\cdot 0.64PrOH$, consists of an open gallophosphate framework with GaO_6 octahedra and PO_4 tetrahedra, forming eight-membered ring channels along the [100], [010] and [001] directions. These channels contain ordered NH_4^+ cations and disordered PrOH molecules as structure-directing agents.

Acknowledgements

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