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Synthesis and crystal structure of a gallium phosphate with 14-ring channels

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The synthesis and crystal structure of a new 14-membered ring gallium oxyfluorophosphate are described: DIPYR-GaPO: $Ga_7P_6O_{28}F_3C_{10}N_2H_{16}$, $M_r = 1343.1$, space group $P\bar{1}$, $a = 12.000(3)$ Å, $b = 13.895(4)$ Å, $c = 10.280(4)$ Å, $\alpha = 101.09(3)°$, $\beta = 100.91(2)°$, $\gamma = 106.41(2)°$, $D_c = 2.83$ g cm^{-3}, $F(000) = 1297$, $R = 2.89\%$, $R_w = 3.63\%$. The product was obtained by hydrothermal synthesis at 170 °C in a reaction using two amines as structure-directing agents in the HF–Ga_2O_3–P_2O_5 system: pyridine and benzylviologen dichloride. The benzylviologen dichloride decomposed during the reaction to form 4,4′-dipyridyl, which was found in the 14-ring channels together with pyridine. Intraframework hydrogen bonding appears to play an important role in determining the shape of the pores.

Microporous molecular sieves are a unique class of crystalline materials due to their uniform pore size distribution and the unique catalytic and separation properties associated with their framework structure. Currently, there is growing demand in the chemical and petroleum industries for molecular sieves with larger pore sizes for catalytic conversions of larger molecules and the separation of more complex mixtures. Until very recently, however, the largest ring opening was a 12-membered ring, as in zeolites L,[1] Beta,[2] Y[3] and mordenite,[4] which limited the size of the pore to approximately 8 Å. The 12-ring silicate barrier was finally broken with the discovery of UTD-1,[5] the first 14-membered ring zeolite, which uses an organometallic structure directing agent, $[(Cp^*)_2Co]OH$ ($Cp^* = Me_5C_5$), in the synthesis. The high silica version of UTD-1 is thermally stable to 1000 °C and the aluminosilicate analogue exhibits the strong acidity normally associated with zeolites.

Large pore molecular sieves were first discovered in the aluminophosphate system where the versatility in the coordination environment of the aluminium center leads to more complex structures with larger pore sizes than those of the aluminosilicate zeolites. Following the discovery of VPI-5,[6] an 18-membered ring aluminophosphate, the number of extra-large pore molecular sieves expanded quickly. Introduction of fluoride into the synthesis by Guth *et al.*[7] led to the formation of cloverite,[8] an interrupted, 20-membered ring framework, where fluorine helps to stabilize the double 4-ring in the structure. Besides stabilizing the 4-membered ring in many alumino- and gallo-phosphates, fluorine is also seen in the coordination sphere of gallium in the ULM-*n*[9] series of gallium oxyfluorophosphates. The largest structure in that series of materials is ULM-5,[10] a 16-membered ring, synthesized from 1,6-diaminohexane and HF, where the fluorine again stabilizes the double 4-membered ring in the structure. Even with the discovery of these very large pore materials, 14-membered rings in the phosphate system have remained relatively rare. The only known 14-membered ring phosphate is $AlPO_4$–8, which has yet to be made synthetically and can only be obtained after the dehydration of VPI-5[11] at elevated temperatures. Ideally, the structure of $AlPO_4$–8 contains circular 14-membered rings, but the adsorption capacity suggests that it is highly faulted.[12] By using two amines in the HF–Ga_2O_3–P_2O_5 system, we report here the synthesis and crystal structure of a new 14-membered ring gallium oxyfluorophosphate, DIPYR-GaPO.

Experimental

Plate-like crystals of DIPYR-GaPO were synthesized from a clear solution having an initial molar oxide composition of 0.87 benzylviologen dichloride : 5.2 HF : 32.1 pyridine : Ga_2O_3 : 1.3 P_2O_5 : 86.3 H_2O. The reagent sources used in the synthesis were as follows: $Ga_2(SO_4)_3$ (Alfa), H_3PO_4, (85 wt.% H_3PO_4, Fisher), HF–pyridine (70 wt.% HF, Aldrich), pyridine (Fisher, PYR), benzylviologen dichloride (Aldrich) and deionized water. The $Ga_2(SO_4)_3$ was first dissolved in the appropriate amount of water before adding the H_3PO_4, HF–pyridine and pyridine. The clear solution was stirred for 5 min before adding the benzylviologen dichloride to the gallium phosphate solution. After the benzylviologen dichloride had completely dissolved, the resulting clear solution (pH = 5.5) was stirred for 45 min. The solution was sealed in a Teflon lined Parr acid digestion bomb and placed in a forced draft oven at 170 °C for 5 days. The product was vacuum filtered, washed with deionized water, rinsed with acetone and air dried. The powder X-ray diffraction pattern of the bulk material contained two phases, PYR-GaPO[13] and DIPYR-GaPO. Since the product was biphasic, we calculated the powder X-ray diffraction pattern of DIPYR-GaPO from the final atomic coordinates (Table 2, later) as shown in Fig. 1. A suitable plate-like crystal from the bulk material was chosen for a single crystal X-ray diffraction study. Data were collected on a Rigaku AFC7S four circle diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.70176$ Å) at 220 K. The unit cell and orientation matrix were determined using automated search and centering routines. The final cell was determined using 20 reflections between $7.33 < 2\theta < 15.87°$. The data were collected using the ω–2θ method with a scan width of $(0.84 + 0.35 \tan\theta)$ and a scan speed of 16° min^{-1}. The weak reflections $[I < 15\sigma(I)]$ were rescanned (maximum 4 scans) and the counts were accumulated to insure good statistics. Data were corrected for decay, Lorentz and polarization effects. The structure was solved using direct methods (SIR-92[14]), and refined in the CRYSTALS suite of programs.[15] Full-matrix least-squares methods were used to refine the framework atoms (Ga, P, O, F) with anisotropic thermal parameters and the organic molecules (C, N) with isotropic thermal parameters. The total occupancy of the pyridine and the 4,4′-dipyridyl molecules that

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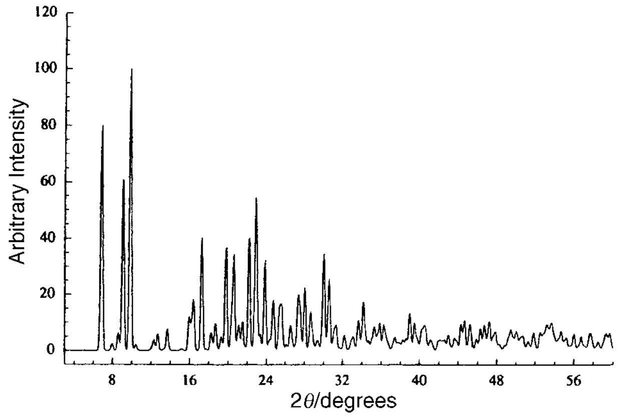

Fig. 1 Calculated powder X-ray diffraction powder of DIPYR-GaPO ($\lambda = 1.541$ Å)

are disordered was fixed to equal 1.0. Restraints were also used to insure the planarity of the aromatic rings. The hydrogen atoms around the ordered 4,4′-dipyridyl, the water and the hydroxide were located from the difference Fourier maps, but were not refined. After all of the atoms were found the following corrections were applied: anomalous scattering and a Tukey and Prince weighting scheme fitted by a 3-term Chebychev polynomial. A summary of the data collection and structure solution for DIPYR-GaPO is given in Table 1.

Results and Discussion

Final atomic positions for DIPYR-GaPO are shown in Table 2 and selected bond distances and angles are shown in Tables 3

Table 1 Summary of the data collection and refinement data for the DIPYR-GaPO structure

name	DIPYR-GaPO
formula	$[Ga_7(PO_4)_6F_3(OH)_2]\cdot 2H_2O\cdot 0.87DIPYR^{2+}\cdot 0.28PYR^{+}$
M_r	1343.1
crystal system	triclinic
space group	$P\bar{1}$
a/Å	12.000(3)
b/Å	13.895(4)
c/Å	10.280(4)
α/°	101.09(3)
β/°	100.91(2)
γ/°	106.41(2)
V/Å^3	1568.9(1)
Z	2
$F(000)$	1296.6
temperature/°C	−53
D_c/g cm^{-3}	2.83
μ/cm^{-1}	63.35
crystal habit	square plate
crystal size/mm	$0.1 \times 0.3 \times 0.6$
2θ/°	$1 < \theta < 60$
number of reflections	7121
unique data	6834
observed reflections, $I > 3\sigma(I)$	5857
R_{int} (%)	2.9
final parameters	624
R_F (%)	2.89
R_{FW} (%)	3.63
S	1.23
weighting scheme	3 term Chebychev weights 1.59, 0.471, 1.14
$(\Delta\rho)_{min}$/e Å^{-3}	0.783
$(\Delta\rho)_{max}$/e Å^{-3}	1.44
absorption correction	psi-scan
T_{min} (%)	69
T_{max} (%)	100
% decay	0.5

Table 2 Final atomic coordinates, equalized temperature factors and occupancies (ESDs in parentheses) for the DIPYR-GaPO structure

atom	x	y	z	U_{eq}/Å^2	occ.
Ga(1)	0.89448(6)	0.55762(6)	0.15017(4)	0.0064	1.0000
Ga(2)	0.81221(6)	0.83612(6)	0.28303(4)	0.0059	1.0000
Ga(3)	0.75081(6)	0.49841(6)	0.50204(4)	0.0039	1.0000
Ga(4)	0.81408(6)	0.21614(6)	0.52485(4)	0.0050	1.0000
Ga(5)	0.29467(6)	0.83554(6)	0.27214(4)	0.0064	1.0000
Ga(6)	0.39097(6)	0.50189(6)	0.13143(4)	0.0076	1.0000
Ga(7)	0.67442(6)	0.77627(6)	0.47853(4)	0.0052	1.0000
P(1)	−0.0340(1)	0.5225(1)	0.3655(1)	0.0051	1.0000
P(2)	0.1094(1)	−0.0227(1)	0.3652(1)	0.0068	1.0000
P(3)	0.6011(1)	0.9701(1)	0.3790(1)	0.0058	1.0000
P(4)	0.4646(1)	0.5112(1)	0.3584(1)	0.0052	1.0000
P(5)	0.1656(1)	0.6227(1)	0.0759(1)	0.0072	1.0000
P(6)	0.6368(1)	0.6496(1)	0.0900(1)	0.0076	1.0000
O(1)	0.9467(4)	0.4877(4)	0.2474(3)	0.0072	1.0000
O(2)	0.0656(4)	0.4569(4)	0.4053(3)	0.0077	1.0000
O(3)	0.0166(4)	0.6595(4)	0.4165(3)	0.0078	1.0000
O(4)	0.8228(4)	0.4791(4)	0.3802(3)	0.0078	1.0000
O(5)	0.1161(4)	0.9062(4)	0.4397(3)	0.0078	1.0000
O(6)	−0.0415(4)	0.9665(4)	0.3142(3)	0.0091	1.0000
O(7)	0.1749(4)	0.9281(4)	0.2774(3)	0.0128	1.0000
O(8)	0.1720(4)	0.1106(4)	0.4168(3)	0.0116	1.0000
O(9)	0.6407(4)	0.1060(4)	0.4378(3)	0.0074	1.0000
O(10)	0.7010(4)	0.9432(4)	0.3142(3)	0.0096	1.0000
O(11)	0.4580(4)	0.9440(4)	0.3049(3)	0.0106	1.0000
O(12)	0.5920(4)	0.8956(4)	0.4505(3)	0.0082	1.0000
O(13)	0.3229(4)	0.4808(4)	0.3770(3)	0.0099	1.0000
O(14)	0.5626(4)	0.4517(4)	0.4106(3)	0.0075	1.0000
O(15)	0.4461(4)	0.4550(4)	0.2404(3)	0.0089	1.0000
O(16)	0.5174(4)	0.6473(4)	0.3884(3)	0.0116	1.0000
O(17)	0.8413(4)	0.4030(4)	0.0379(3)	0.0100	1.0000
O(18)	0.0242(4)	0.6234(4)	0.0938(3)	0.0109	1.0000
O(19)	0.2637(4)	0.7484(4)	0.1354(3)	0.0112	1.0000
O(20)	0.2206(4)	0.5294(4)	0.1177(3)	0.0120	1.0000
O(21)	0.7202(4)	0.7793(4)	0.1439(3)	0.0097	1.0000
O(22)	0.5008(4)	0.6338(4)	0.1208(3)	0.0136	1.0000
O(23)	0.3910(4)	0.3712(4)	0.0259(3)	0.0110	1.0000
O(24)	0.7092(4)	0.5584(4)	0.1182(3)	0.0110	1.0000
O(25)	0.7778(4)	0.7581(4)	0.3751(3)	0.0106	1.0000
O(26)	0.4302(4)	0.2206(4)	0.4092(3)	0.0113	1.0000
O(27)	0.8940(4)	0.1851(4)	0.3986(3)	0.0126	1.0000
O(28)	0.2678(4)	0.7434(4)	0.3558(3)	0.0101	1.0000
F(1)	0.9274(3)	0.7206(3)	0.2440(2)	0.0108	1.0000
F(2)	0.7284(3)	0.3300(3)	0.4787(2)	0.0073	1.0000
F(3)	0.2351(3)	0.3354(3)	0.4760(2)	0.0076	1.0000
N(1)[a]	0.6556(6)	0.2698(6)	0.2039(4)	0.024(1)	1.0000
N(7)[a]	0.112(1)	0.2740(9)	0.2071(5)	0.054(1)	0.73(2)
N(13)[a]	0.145(3)	0.273(2)	0.199(2)	0.025(6)	0.28(2)
C(2)[a]	0.5352(7)	0.0577(7)	0.0434(5)	0.024(1)	1.0000
C(3)[a]	0.5594(7)	0.1680(7)	0.0268(5)	0.025(1)	1.0000
C(4)[a]	0.6190(7)	0.2727(7)	0.1084(5)	0.024(1)	1.0000
C(5)[a]	0.6375(9)	0.1670(8)	0.2232(7)	0.036(2)	1.0000
C(6)[a]	0.578(1)	0.0603(9)	0.1442(7)	0.043(2)	1.0000
C(8)[a]	0.0608(9)	0.2721(8)	0.1071(6)	0.045(2)	1.0000
C(9)[a]	0.1872(9)	0.1934(8)	0.2244(5)	0.055(3)	1.0000
C(10)[a]	0.086(2)	0.191(1)	0.0244(5)	0.054(4)	0.73(2)
C(11)[a]	0.215(1)	0.114(1)	0.1419(8)	0.071(5)	0.73(2)
C(12)[a]	0.166(2)	0.114(1)	0.0420(6)	0.074(6)	0.73(2)
C(14)[a]	0.031(2)	0.058(2)	0.042(2)	0.022(6)	0.28(2)
C(15)[a]	0.130(4)	0.069(3)	0.129(3)	0.042(8)	0.28(2)
C(16)[a]	0.005(4)	0.167(4)	0.033(3)	0.05(1)	0.28(2)
H(1)	0.6331	0.3447	0.0973	0.0500	1.0000
H(2)	0.5359	0.1704	−0.0383	0.0500	1.0000
H(3)	0.5654	−0.0105	0.1580	0.0500	1.0000
H(4)	0.6657	0.1672	0.2891	0.0500	1.0000
H(5)	0.8503	0.7245	0.3950	0.0500	1.0000
H(6)	0.3447	0.7238	0.3782	0.0500	1.0000
H(7)	0.4997	0.1835	0.4170	0.0500	1.0000
H(8)	0.9703	0.2308	0.4073	0.0500	1.0000
H(9)	0.9156	0.1198	0.3770	0.0500	1.0000
H(10)	0.7084	0.3318	0.2491	0.0500	1.0000
H(11)	0.4831	0.2930	0.4139	0.0500	1.0000

[a] Isotropic temperature factor.

Table 3 Bond distances (Å) with ESDs for the DIPYR-GaPO structure

Ga(1)—O(1)	1.837(4)	Ga(2)—O(6)	1.836(4)
Ga(1)—O(17)	1.962(4)	Ga(2)—O(10)	1.891(4)
Ga(1)—O(18)	1.839(4)	Ga(2)—O(21)	1.856(4)
Ga(1)—O(24)	1.874(4)	Ga(2)—O(25)	1.841(4)
Ga(1)—F(1)	1.947(3)	Ga(2)—F(1)	2.016(3)
Ga(3)—O(2)	1.953(4)	Ga(4)—O(3)	1.925(4)
Ga(3)—O(4)	1.957(4)	Ga(4)—O(5)	1.894(4)
Ga(3)—O(13)	1.956(4)	Ga(4)—O(9)	1.942(4)
Ga(3)—O(14)	1.982(4)	Ga(4)—O(27)	2.058(4)
Ga(3)—F(2)	1.915(3)	Ga(4)—O(28)	1.992(4)
Ga(3)—F(3)	1.902(3)	Ga(4)—F(2)	1.948(3)
Ga(5)—O(7)	1.806(4)	Ga(6)—O(15)	1.798(4)
Ga(5)—O(11)	1.806(4)	Ga(6)—O(20)	1.827(4)
Ga(5)—O(19)	1.833(4)	Ga(6)—O(22)	1.823(4)
Ga(5)—O(28)	1.846(4)	Ga(6)—O(23)	1.825(4)
Ga(7)—O(8)	1.912(4)		
Ga(7)—O(12)	1.890(4)		
Ga(7)—O(16)	1.939(4)		
Ga(7)—O(25)	1.942(4)		
Ga(7)—O(26)	2.063(4)		
Ga(7)—F(1)	1.947(3)		
P(1)—O(1)	1.548(4)	P(2)—O(5)	1.522(4)
P(1)—O(2)	1.520(4)	P(2)—O(6)	1.543(4)
P(1)—O(3)	1.534(4)	P(2)—O(7)	1.539(4)
P(1)—O(4)	1.539(4)	P(2)—O(8)	1.508(4)
P(3)—O(9)	1.537(4)	P(4)—O(13)	1.523(4)
P(3)—O(10)	1.517(4)	P(4)—O(14)	1.530(4)
P(3)—O(11)	1.547(4)	P(4)—O(15)	1.554(4)
P(3)—O(12)	1.521(4)	P(4)—O(16)	1.525(5)
P(5)—O(17)	1.518(4)	P(6)—O(21)	1.519(4)
P(5)—O(18)	1.523(4)	P(6)—O(22)	1.534(4)
P(5)—O(19)	1.542(4)	P(6)—O(23)	1.529(4)
P(5)—O(20)	1.548(4)	P(6)—O(24)	1.531(4)

and 4. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/98. The asymmetric unit is shown in Fig. 2; by connecting these building units together through a series of 3- and 4-membered rings, a 14-membered ring channel parallel to the *a* axis is created (Fig. 3). The framework stoichiometry is $[Ga_7(PO_4)_6F_3(OH)_2]^{2-}$ and is balanced by the extra-framework organic cations. The framework of DIPYR-GaPO is quite different from any of the others reported in the literature. It does not contain the typical building unit, $[Ga_3(PO_4)_3F_2]^{2-}$, that is seen in TREN-GaPO,[16] DAO-GaPO[13] (DAO = diaminooctane) and the ULM-*n*[9] series of materials. The framework consists of 4, 5 and 6 coordinate gallium (Fig. 3); the tetrahedrally coordinated atoms, Ga(5) and Ga(6), have only oxygen in the coordination sphere, while the five- and six-coordinate metal centers are bonded to at least one fluorine

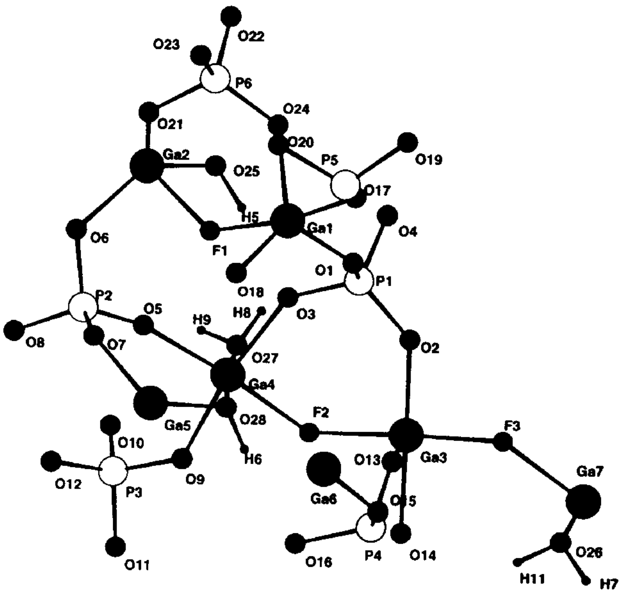

Fig. 2 Asymmetric unit of DIPYR-GaPO

Table 4 Bond angles (°) with ESDs for the DIPYR-GaPO structure

O(1)—Ga(1)—O(17)	92.0(2)	O(6)—Ga(2)—O(10)	88.8(2)
O(1)—Ga(1)—O(18)	119.1(2)	O(6)—Ga(2)—O(21)	112.0(2)
O(17)—Ga(1)—O(18)	92.4(2)	O(10)—Ga(2)—O(21)	91.9(2)
O(1)—Ga(1)—O(24)	116.0(2)	O(6)—Ga(2)—O(25)	123.4(2)
O(17)—Ga(1)—O(24)	86.8(2)	O(10)—Ga(2)—O(25)	96.5(2)
O(18)—Ga(1)—O(24)	124.9(2)	O(21)—Ga(2)—O(25)	124.0(2)
O(1)—Ga(1)—F(1)	97.8(2)	O(6)—Ga(2)—F(1)	91.7(2)
O(17)—Ga(1)—F(1)	169.7(2)	O(10)—Ga(2)—F(1)	177.8(2)
O(18)—Ga(1)—F(1)	85.6(2)	O(21)—Ga(2)—F(1)	85.9(2)
O(24)—Ga(1)—F(1)	86.1(2)	O(25)—Ga(2)—F(1)	85.0(2)
O(2)—Ga(3)—O(4)	92.3(2)	O(3)—Ga(4)—O(5)	96.3(2)
O(2)—Ga(3)—O(13)	88.3(2)	O(3)—Ga(4)—O(9)	166.0(2)
O(4)—Ga(3)—O(13)	179.1(2)	O(5)—Ga(4)—O(9)	93.7(2)
O(2)—Ga(3)—O(14)	178.6(2)	O(3)—Ga(4)—O(27)	81.1(2)
O(4)—Ga(3)—O(14)	89.0(2)	O(5)—Ga(4)—O(27)	89.6(2)
O(13)—Ga(3)—O(14)	90.4(2)	O(9)—Ga(4)—O(27)	89.2(2)
O(2)—Ga(3)—F(2)	93.6(2)	O(3)—Ga(4)—O(28)	98.1(2)
O(4)—Ga(3)—F(2)	88.4(2)	O(5)—Ga(4)—O(28)	94.8(2)
O(13)—Ga(3)—F(2)	92.2(2)	O(9)—Ga(4)—O(28)	90.8(2)
O(14)—Ga(3)—F(2)	85.9(2)	O(27)—Ga(4)—O(28)	175.6(2)
O(2)—Ga(3)—F(3)	88.6(2)	O(3)—Ga(4)—F(2)	88.7(2)
O(4)—Ga(3)—F(3)	92.6(2)	O(5)—Ga(4)—F(2)	174.6(2)
O(13)—Ga(3)—F(3)	86.8(2)	O(9)—Ga(4)—F(2)	81.0(2)
O(14)—Ga(3)—F(3)	91.9(2)	O(27)—Ga(4)—F(2)	89.3(2)
F(2)—Ga(3)—F(3)	177.6(2)	O(28)—Ga(4)—F(2)	86.3(2)
O(7)—Ga(5)—O(11)	102.8(2)	O(15)—Ga(6)—O(20)	113.9(2)
O(7)—Ga(5)—O(19)	106.0(2)	O(15)—Ga(6)—O(22)	118.2(2)
O(11)—Ga(5)—O(19)	105.3(2)	O(20)—Ga(6)—O(22)	105.3(2)
O(7)—Ga(5)—O(28)	108.6(2)	O(15)—Ga(6)—O(23)	100.5(2)
O(11)—Ga(5)—O(28)	118.4(2)	O(20)—Ga(6)—O(23)	111.1(2)
O(19)—Ga(5)—O(28)	114.4(2)	O(22)—Ga(6)—O(23)	107.7(2)
O(8)—Ga(7)—O(12)	94.1(2)		
O(8)—Ga(7)—O(16)	170.6(2)		
O(12)—Ga(7)—O(16)	92.4(2)		
O(8)—Ga(7)—O(25)	92.4(2)		
O(12)—Ga(7)—O(25)	98.8(2)		
O(16)—Ga(7)—O(25)	93.2(2)		
O(8)—Ga(7)—O(26)	88.2(2)		
O(12)—Ga(7)—O(26)	87.2(2)		
O(16)—Ga(7)—O(26)	85.4(2)		
O(25)—Ga(7)—O(26)	173.9(2)		
O(8)—Ga(7)—F(3)	80.8(2)		
O(12)—Ga(7)—F(3)	173.4(2)		
O(16)—Ga(7)—F(3)	92.2(2)		
O(25)—Ga(7)—F(3)	85.6(2)		
O(26)—Ga(7)—F(3)	88.5(2)		
O(1)—P(1)—O(2)	107.2(2)	O(5)—P(2)—O(6)	110.0(2)
O(1)—P(1)—O(3)	110.3(2)	O(5)—P(2)—O(7)	111.4(2)
O(2)—P(1)—O(3)	112.8(2)	O(6)—P(2)—O(7)	106.8(2)
O(1)—P(1)—O(4)	105.7(2)	O(5)—P(2)—O(8)	113.7(2)
O(2)—P(1)—O(4)	111.5(2)	O(6)—P(2)—O(8)	104.5(2)
O(3)—P(1)—O(4)	109.2(2)	O(7)—P(2)—O(8)	110.0(2)
O(9)—P(3)—O(10)	108.6(2)	O(13)—P(4)—O(14)	111.7(2)
O(9)—P(3)—O(11)	105.1(2)	O(13)—P(4)—O(15)	106.6(2)
O(10)—P(3)—O(11)	108.0(2)	O(14)—P(4)—O(15)	106.1(2)
O(9)—P(3)—O(12)	112.4(2)	O(13)—P(4)—O(16)	109.5(2)
O(10)—P(3)—O(12)	112.9(2)	O(14)—P(4)—O(16)	114.4(2)
O(11)—P(3)—O(12)	109.4(2)	O(15)—P(4)—O(16)	108.1(2)
O(17)—P(5)—O(18)	110.2(2)	O(21)—P(6)—O(22)	108.6(2)
O(17)—P(5)—O(19)	107.7(2)	O(21)—P(6)—O(23)	106.4(2)
O(18)—P(5)—O(19)	108.8(2)	O(22)—P(6)—O(23)	109.8(2)
O(17)—P(5)—O(20)	111.9(2)	O(21)—P(6)—O(24)	113.4(2)
O(18)—P(5)—O(20)	109.4(2)	O(22)—P(6)—O(24)	108.1(2)
O(19)—P(5)—O(20)	108.8(2)	O(23)—P(6)—O(24)	110.6(2)

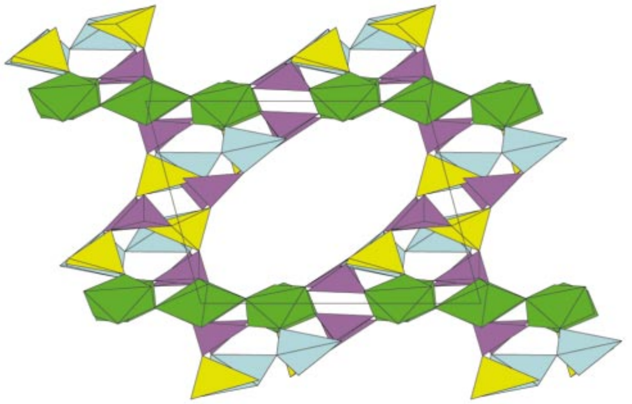

Fig. 3 Polyhedral representation of the DIPYR-GAPO framework viewed along the [001] direction. Phosphate-centred tetrahedra are coloured magenta, and 4-, 5- and 6-coordinate gallium polyhedra are coloured yellow, cyan and green respectively.

atom. The fluorine in the coordination sphere seems to be necessary to stabilize the high-coordination environment around the gallium centers and may increase the framework rigidity. There are two oxygen bridges [O(25) and O(28)] between gallium atoms, which on the basis of their refined temperature factors and the appearance of hydrogens in the difference Fourier map, suggest that they are Ga–(OH)–Ga links. To our knowledge, this feature has not been seen in any other gallium phosphate open framework material. Even though this species is present in the framework, the coordination environment of the gallium atoms remains quite regular. The trigonal bipyramidal gallium atoms show the expected variation in bond distances; axial Ga–O lengths are significantly longer than the equatorial ones. Both the octahedral and tetrahedral gallium coordination environments are quite regular. All of the linkages from the tetrahedral phosphate species are oxygens that bridge to gallium atoms (average P–O distance = 1.531 Å, range of O–P–O angles = 104.5–114.4°).

There are two templates present in the channels of the DIPYR-GaPO: 4,4′-dipyridyl, formed from the decomposition of benzylviologen dichloride, and pyridine (Fig. 4). Since the synthesis was done under acidic conditions and the framework is negatively charged, it is reasonable to assume that both of the organic molecules are protonated. The cations occupy two sites in the channels, one of which is occupied solely by 4,4′-dipyridyl, and one that is disordered with approximately 70% 4,4′-dipyridyl and 30% pyridine. The two different sites are stacked alternately along the channel as shown in Fig. 5. The hydrogen atoms of the 4,4′-dipyridyl were located from the difference Fourier maps indicating that there is relatively strong hydrogen bonding to one of the framework oxygens [O(4)···H–N(1) distance of 2.103(7) Å]. The hydrogen atoms on the disordered organics could not be found, but the nitrogen atom positions, which are almost coincident, indicate that there is similar hydrogen bonding at this site as well [N(7)···O(13) distance of 3.02(2) Å, N(13)···O(13) distance of 2.97(2) Å].

Another unique feature of this structure is the intraframework hydrogen bonding. Two water molecules associated with O(26) and O(27), which form part of the coordination spheres of the octahedral galliums [Ga(4) and Ga(7)], make strong hydrogen bonds to other oxygens in the framework. The hydrogen atoms on O(26) bond to O(14) and O(9) [1.942(2) Å and 1.885(3)Å, respectively] and a hydrogen on O(27) bonds to O(6) [1.973(3) Å], suggesting that the internal hydrogen bonding within the framework may aid in determining the shape of the pore. The Ga–(OH)–Ga linkages also seem to

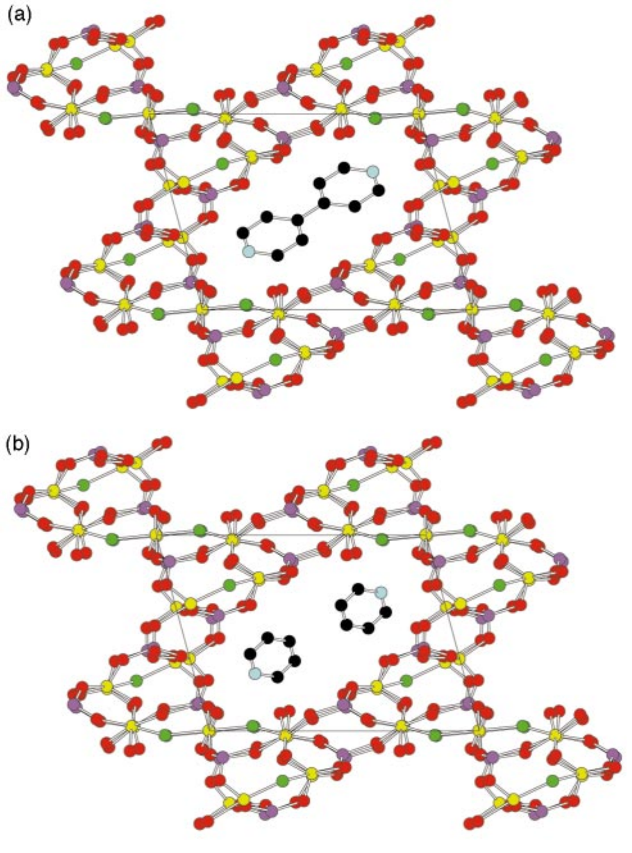

Fig. 4 The 14-ring of DIPYR-GaPO as viewed along the [100] direction showing (a) the orientation of the 4,4′-dipyridyl molecules and (b) the orientation of the pyridine molecules inside the channels. Ga, P, O, F, C and N atoms are shown as yellow, magenta, red, green, black and cyan spheres respectively.

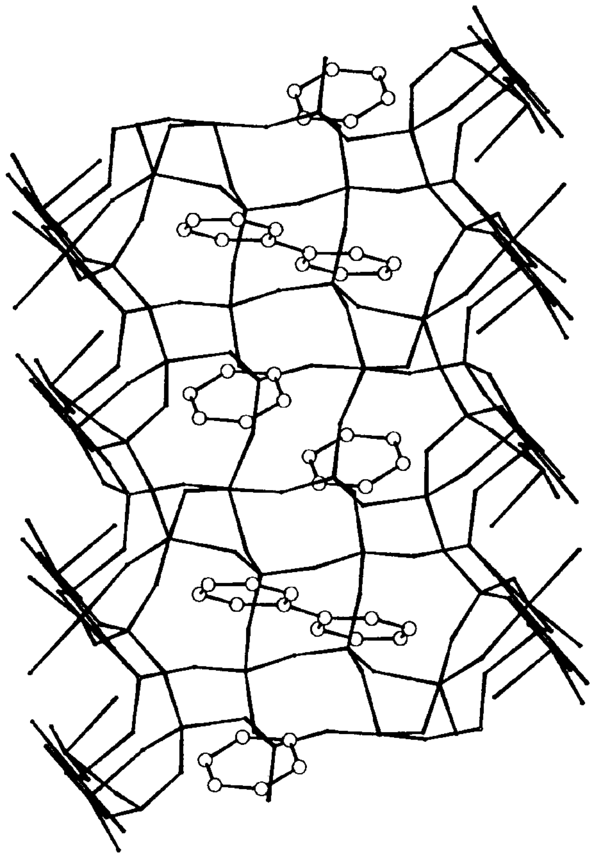

Fig. 5 Stacking sequence of 4,4′-dipyridyl and pyridine as viewed along the [010] direction

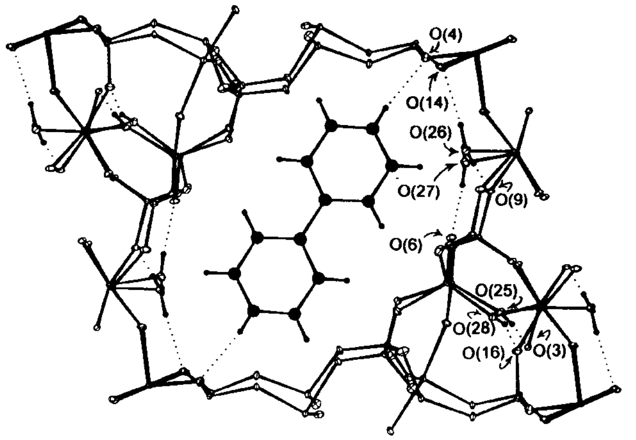

Fig. 6 Hydrogen bonding scheme in the 14-ring channel of DIPYR-GaPO showing the 4,4′-dipyridyl, water and Ga–(OH)–Ga coordination to the framework oxygens. For clarity only the oxygen atoms involved in the hydrogen bonding are labeled. Thermal ellipsoids for the framework atoms are shown at the 50% probability level.

form slightly longer hydrogen bonds to other framework oxygen atoms [O(25)–H···O(3) distance of 2.014(3) Å and O(28)–H···O(16) distance of 2.147(3) Å], but still seem to be important in determining the pore structure. The hydrogen bonding in the structure is shown in Fig. 6. Intramolecular hydrogen bonding, like that in DIPYR-GaPO, is also important in many biological and organic systems. For example, the synthesis of mesomolecular dendritic assemblies uses internal hydrogen bonding within molecules as well as hydrogen bonding between assemblies of molecules to control the size and shape of the dendritic network.[17]

4,4′-Dipyridyl, formed from the decomposition of benzylviologen dichloride, seems to be the structure directing agent in the synthesis of DIPYR-GaPO, but when 4,4′-dipyridyl and pyridine are used in the synthesis, we obtained crystals of an organometallic 4,4′-dipyridyl gallium oxide phase [$a = 15.522(2)$ Å, $b = 3.8422(2)$ Å, $c = 10.731(1)$ Å, $\beta = 133.736(7)°$, $V_{\text{cell}} = 462.4(1)$ Å^3]. This structure is composed of chains of gallium octahedra hydrogen bonded together through a 4,4′-dipyridyl molecule. The formation of this phase suggests that both pyridine and the *in situ* formation of 4,4-dipyridyl are necessary for the formation of DIPYR-GaPO. In the synthesis of DIPYR-GaPO, the 4,4′-dipyridyl seems to be acting as the structure directing agent since it fits quite tightly in the pore and hydrogen bonds strongly to the framework oxygens (Fig. 5) while the pyridine merely seems to fill any residual void volume. The use of two amines in the synthesis seems to be a facile way to begin to control the shape and size of the channels.

Thermogravimetric analysis of the material shows one thermal event at *ca.* 400 °C, which is presumably due to loss of the organic templates from the structure. Since the powdered sample contains two phases, this weight loss could not be quantified. All attempts to try to remove the organics under highly oxidizing conditions, *i.e.* flowing oxygen, at 500 °C result in the collapse of the framework. Low temperature extraction routes to remove the organics have resulted in removal of some of the organics without degrading the framework. Further attempts using O_2 plasmas are currently underway.

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