Synthesis and Crystal Structure of IM-6, a New Open Framework Cobalt–Gallium Phosphate with Ten- and Twelve-Membered Pore Openings

Ludovic Josien,[a] Angélique Simon-Masseron,*[a] Volker Gramlich,[b] Joël Patarin,[a] and Loïc Rouleau[c]

Abstract: A new three-dimensional microporous cobalt–gallium phosphate, named IM-6, has been synthesized under solvothermal conditions with an N-substituted piperazine as organic template. The structure was solved by single-crystal X-ray diffraction (triclinic, $P\bar{1}$, $a = 9.848(20)$, $b = 12.470(32)$, $c = 12.603(28)$ Å, $\alpha = 63.47(16)^\circ$, $\beta = 74.56(16)^\circ$, $\gamma = 76.03(17)^\circ$). IM-6 exhibits a new framework topology. The inorganic framework is built up of MO_4 (M = Co, Ga) and PO_4 tetrahedra. It displays a two-dimensional interconnected channel system running along the $[0\bar{1}1]$ and [100] directions and delimited by ten- and twelve-membered ring openings, respectively.

Keywords: cobalt · gallium · piperazine · phosphate · solvothermal synthesis · structure elucidation

Introduction

Since the pioneering work by Union Carbide Corporation in 1982[1] on aluminophosphates with the development of the $AlPO_4$-n series, the field of microporous metallophosphates has not dried up. The family of the gallophosphates has also given a wide range of new structures. As with aluminophosphates, gallophosphates can also be partly substituted by transition metals.

Even if Ga atoms can adopt the five- and six-coordinate states in gallophosphates, it is unusual that the substituted gallophosphates (MeGaPOs) possess such metal coordination. Indeed, with the exceptions of compounds containing the cation Mn^{2+},[2–4] which can easily adopt various coordination states and the $[NH_4][MeGa_2P_3O_{12}(H_2O)_2]$ structure with Me = Co, Zn, Mn, Mg, Fe,[5, 6] all MeGaPOs are only composed four-coordinate metal centers; among them, some have zeolitic frameworks. Nevertheless original structures like CGF (CoGaPO-5),[7] CGS (CoGaPO-6),[8] SBS (UCSB-6) and SBT (UCSB-10)[9] structure types are specific to metallophosphates. Furthermore it is noteworthy that a large number of substituted gallophosphates has been prepared in quasi nonaqueous medium with an organic solvent, mainly in the presence of ethylene glycol.[10]

The present paper reports the synthesis, characterization, and structure determination of a new three-dimensional cobaltgallophosphate named IM-6 (Institut Français du Pétrole-Mulhouse number 6). It was prepared by solvothermal synthesis in a quasi nonaqueous medium in the presence of 1-methylpiperazine as organic template. This new material, which possesses an original structure, displays a two-dimensional system of interconnected channels delimited by twelve- and ten-membered-ring openings. This new CoGaPO was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray emission mapping, and elemental and thermal analyses.

Experimental Section

Syntheses: IM-6 was synthesized under solvothermal conditions in ethylene glycol (EG) (SDS, 99 %) as solvent. The others chemical sources used in the synthesis were an amorphous gallium oxide hydroxide, which was prepared by heating a gallium nitrate solution (Rhône-Poulenc) at 250 °C for 24 h, a hydrated cobalt carbonate (Aldrich, 7 wt % of water), phosphoric acid (Labosi, 85 % in water), fumed silica (for the synthesis of cobaltsilicogallophosphate; Cab-O-Sil), and an amine (1-methylpiperazine (MPIP) (Aldrich, 99 %), 1-ethylpiperazine (EPIP) (Aldrich, 98 %) or 1,4-dimethylpiperazine (DMPIP) (Aldrich, 98 %)).

The cobaltgallophosphate IM-6 crystallizes from a mixture with the following molar composition: $1\,Ga_2O_3/2\,CoCO_3/1\,P_2O_5/1$ amine$/4\,H_2O/50$ EG. As an example, for sample A (Table 1), the gel was prepared by adding under stirring the gallium source (0.28 g) to the cobalt carbonate (0.32 g) dissolved in ethylene glycol (3.85 g). After a homogenization time

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Table 1. Synthesis conditions of IM-6. Starting molar gel composition: $1\,Ga_2O_3/2\,CoCO_3/1\,P_2O_5/1\,amine/4\,H_2O/50\,EG/\times SiO_2$.

Sample	Cobalt source	Amine source	SiO_2 (x)	XRD results
A	$CoCO_3$	MPIP	0	IM-6
B	$CoCO_3$	EPIP	0	IM-6
C	$CoCO_3$	DMPIP	0	IM-6
D	$CoCO_3$	MPIP	1	CoGaPSO IM-6

of 10 minutes, phosphoric acid (0.29 g) and 1-methylpiperazine (0.13 g) were successively introduced. The resulting gel was mixed at room temperature for one hour and transferred into a 20 mL PTFE-lined stainless steel autoclave. The crystallization was carried out at 180 °C under static conditions. After eight days of heating, the product was recovered, washed with distilled water in an ultrasonic bath for a few minutes, and dried at 60 °C overnight.

Characterization: The powder XRD patterns were obtained with $Cu_{K\alpha 1}$ radiation on a STOE STADI-P diffractometer equipped with a curved germanium (111) primary monochromator and a linear position sensitive detector.

The morphology and size of the crystals were determined by scanning electron microscopy by using a Philips XL30 microscope. The X-ray emission mappings were obtained with an Oxford EDX microanalyser coupled to the previous microscope.

The amounts of Co, Ga, and P were determined by scanning electron microprobe analysis on a Castaing type (CAMEBAX) electron microscope.

The ^1H liquid NMR spectrum was recorded on a Bruker AC250 spectrometer. It allowed the determination of the amount of organics occluded in the structure. The sample was prepared by dissolution of known amounts of IM-6 and 1,4-dioxane (internal reference) in hydrochloric acid.[11] Cobalt hydroxide was precipitated at pH 7 and separated from the solution to free from the quadripolar effects of cobalt.

For the structure determination, a single crystal fragment with dimensions $100 \times 70 \times 50$ µm³ was selected from the batch and mounted on a Picker STOE diffractometer. 2717 reflections were recorded from 4 up to 50 °θ (with $Cu_{K\alpha}$ radiation) in omega scan mode of which 1716 fulfilled the condition $I > 2\sigma(I)$. A summary of the experimental and crystallographic data is reported in Table 2.

The diffuse reflectance UV-visible spectrum was recorded on an UVIKON 943 spectrophotometer equipped with a diffuse reflectance unit with a scan speed of 200 nm min^{-1} in a range of 200–900 nm. Barium sulfate was used as a white standard. The spectrum is represented as the Kubelka–Munk function versus wavenumber.

Results and Discussion

Synthesis and microprobe analysis: The most characteristic synthesis results are summarized in Table 1. IM-6 can be obtained with different N-substituted piperazines (samples A to C). The deep blue crystals of IM-6 have a platelet-like morphology and their size ranges from $30 \times 10 \times 10$ to $150 \times 70 \times 50$ µm (see Figure 1a). The incorporation of silicon into the inorganic framework was investigated. A silicon source (Cab-O-Sil fumed silica) was added to the synthesis mixture and a CoGaPSO material with the IM-6 structure crystallized (sample D).

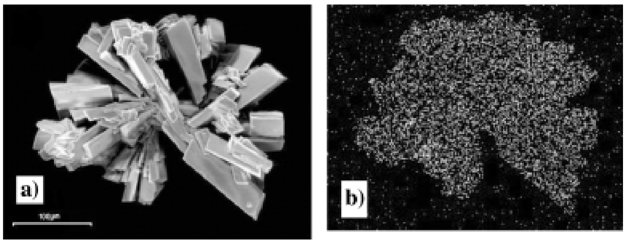

Figure 1. a) Scanning electron micrograph and b) cobalt X-ray emission mapping of the cobaltgallophosphate IM-6 (sample A).

Table 2. Summary of the experimental and crystallographic data of the cobaltgallophosphate IM-6 (sample A).

formula	$[Co_2Ga_3(PO_4)_5](C_5H_{13}N_2) \cdot H_2O$
crystal system	triclinic
space group	$P\bar{1}$
a [Å]	9.848(20)
b [Å]	12.470(32)
c [Å]	12.603(28)
α[°]	63.47(16)
β[°]	74.56(16)
γ[°]	76.03(17)
M_r [g mol^{-1}]	924.09
ρ_{calcd}	2.30
V [Å^3]	1321.2(52)
Z	2
crystal size [µm]	$100 \times 70 \times 50$
diffractometer	PICKER 4-circle Stoe
radiation source/λ[Å]	$Cu_{K\alpha}$/1.54178
μ [mm^{-1}]	16.773
absorption correction	not applied
$F(000)$	890
T [K]	293(2)
θ range [°]	4.00 to 50.00
index ranges	$-9 \leq h \leq 9$
	$-10 \leq k \leq 12$
	$0 \leq l \leq 12$
independent reflections	2717
observed reflections [$I > 2\sigma(I)$]	1716
data/restraints/parameters	2717/74/348
residuals (observed data) [$I > 2\sigma(I)$]	$R1 = 0.0621$, $wR2 = 0.1523$
residuals (all data)	$R1 = 0.1164$, $wR2 = 0.1860$
goodness-of-fit (all data)	0.995
largest difference peak/hole [e Å^{-3}]	0.962/ − 0.957

The repartition of the various elements, especially that of cobalt and silicon, was checked by $Co_{K\alpha}$ and $Si_{K\alpha}$ X-ray emission mappings. Both cobalt and silicon were found homogeneously distributed through the crystals of IM-6 (samples A and D). No concentration gradient was observed (see Figures 1 and 2).

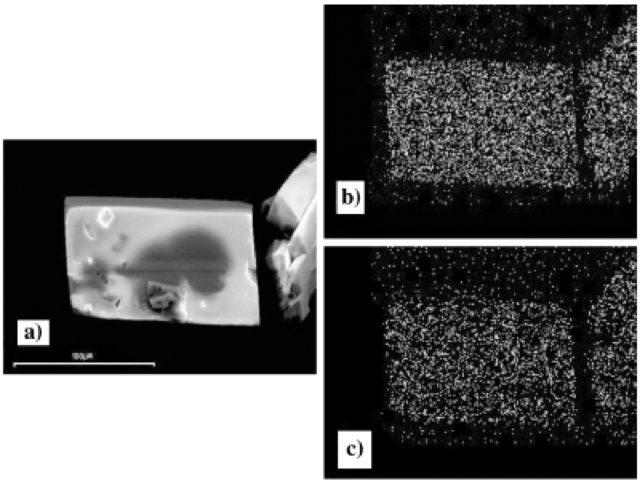

Figure 2. a) Scanning electron micrograph, b) cobalt X-ray emission mapping, and c) silicon X-ray emission mapping of the Si containing cobaltgallophosphate IM-6 (sample D).

Microprobe analysis was performed on several crystals of IM-6 (sample A) in order to determine the Ga/Co molar ratio. From these analyses, the as-synthesized IM-6 sample has the following composition (wt%): Co 12.5(13), Ga 21.6(8), P 16.3(6) which leads to a Ga/Co and (Ga + Co)/P molar ratios equal to 3:2 and 1, respectively. The (Ga + Co)/P ratio is in agreement with the theoretical composition obtained from the structure determination. According to the whole of the analyses (microprobe and TG analyses, structure determination (see below)) the chemical formula of sample A is as follows: $[Co_2Ga_3(PO_4)_5](C_5H_{13}N_2) \cdot H_2O$.

Diffuse reflectance spectroscopy and XRD analysis: To evidence the oxidation state of Co in the framework, diffuse reflectance spectroscopy was carried out (Figure 3). The spectrum displays a strong triplet band (maxima at 15900, 17200 and 18400 cm^{-1}) characteristic of tetrahedrally coordinated Co^{II}. Three hypotheses have been reported by Verberckmoes et al.[12] to explain the splitting of the band in three components. This band can be unambiguously assigned to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition.[13] This analysis is in agreement with the structure determination (see below).

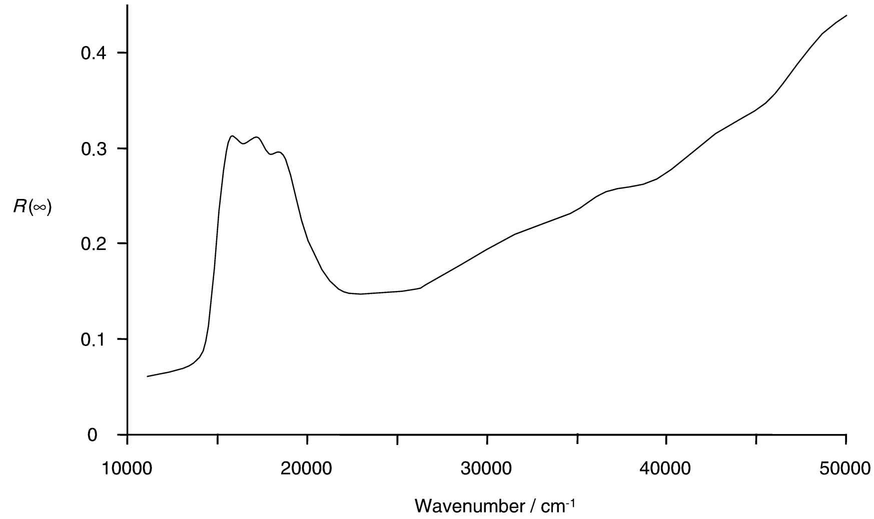

Figure 3. Diffuse reflectance UV-visible spectrum of the cobaltgallophosphate IM-6 (sample A).

The powder XRD pattern of IM-6 (Figure 4 top) was indexed in the triclinic space group $P\bar{1}$ (no. 2) with the following unit cell parameters: $a = 9.848(20)$, $b = 12.470(32)$, $c = 12.603(28)$ Å, $\alpha = 63.47(16)°$, $\beta = 74.56(16)°$, $\gamma = 76.03(17)°$.

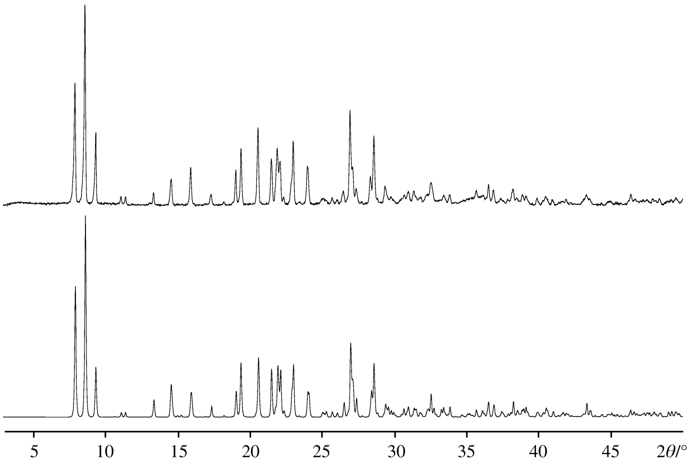

Figure 4. Top: Experimental XRD pattern of IM-6 (Sample A). Bottom: simulated XRD pattern of IM-6 calculated from the single-crystal structure data.

Structure determination and thermal analysis: The structure determination was performed on a single crystal of cobaltgallophosphate (sample A) prepared in the presence of MPIP as organic template.

The structure analysis was performed with SHELX programs. From direct methods by using SHELXS-86,[14] the positions of phosphorus and gallium (or cobalt) atoms were revealed. The respective attribution of Co and Ga atom positions was not possible. Indeed their nearly identical electron environment did not allow us to distinguish these atoms. With the exception of the disordered organic molecule present in the twelve-membered ring channels, the remaining C, N, and O atoms were located from successive Fourier maps using SHELXL-93.[15] Then, the disordered electron density was filled with a model of the 1-methylpiperazine.

The resulting atomic coordinates including the equivalent isotropic displacement parameters are reported in Table 3. The selected bond lengths and angles are given in Tables 4 and 5, respectively. The amine model and the water molecule were placed with geometrical constraints. All the other atoms were refined with anisotropic displacement parameters. It finally led to the following reliability factors: $R_1 = 0.0621$ ($R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$) and $wR_2 = 0.1523$ ($R_2 = \{\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2\}^{1/2}$) for $I > 2\sigma(I)$. The high reliability factor values can be explained by the presence of the disorder in the twelve-membered-ring channels. For comparison, the simulated XRD pattern of IM-6 calculated from structure data is given in Figure 4 (bottom).

To get a better insight of the organic species occluded in the IM-6 structure, ^1H liquid NMR spectroscopy was performed after dissolution of the sample. The presence of 1-methylpiperazine and of an unidentified species was evidenced. The latter molecule could be a piperazine molecule or a piperazine derivative resulting from the partial decomposition of the 1-methylpiperazine as observed for instance in Mu-18.[16] It is possible that the presence of both 1-methylpiperazine and the derivative could explain the partial disorder observed in the twelve-membered-ring channels, which was modeled by a 1-methylpiperazine molecule.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters [Å^2] for the cobaltgallophosphate IM-6 (sample A): standard deviations in brackets.

Atom	*x*	*y*	*z*	*U*(eq)	Occupancy
Ga1	0.2002(2)	0.88246(15)	0.51811(15)	0.0239(5)	0.60
Ga2	– 0.0973(2)	0.59856(15)	0.83766(14)	0.0233(5)	0.60
Ga3	– 0.3669(2)	0.8381(2)	0.4940(2)	0.0360(5)	0.60
Ga4	– 0.6079(2)	0.6602(2)	0.9031(2)	0.0276(5)	0.60
Ga5	– 0.5314(2)	0.4647(2)	0.6900(2)	0.0216(12)	0.60
Co1	0.2002(2)	0.88246(15)	0.51811(15)	0.0239(5)	0.40
Co2	– 0.0973(2)	0.59856(15)	0.83766(14)	0.0233(5)	0.40
Co3	– 0.3669(2)	0.8381(2)	0.4940(2)	0.0360(5)	0.40
Co4	– 0.6079(2)	0.6602(2)	0.9031(2)	0.0276(5)	0.40
Co5	– 0.5314(2)	0.4647(2)	0.6900(2)	0.0216(12)	0.40
P1	– 0.1157(4)	0.8306(3)	0.5996(3)	0.0271(9)	
P2	– 0.6384(4)	0.8967(3)	0.6851(3)	0.0324(10)	
P3	– 0.3387(4)	0.4913(3)	0.8294(3)	0.0292(9)	
P4	– 0.5482(4)	0.6979(3)	0.4512(3)	0.0265(9)	
P5	– 0.7898(3)	0.4894(3)	0.8831(3)	0.0250(9)	
O1	0.3449(10)	0.8111(9)	0.4332(9)	0.047(3)	
O2	0.2367(11)	0.8668(9)	0.6602(8)	0.056(3)	
O3	0.1828(13)	1.0447(8)	0.4144(9)	0.064(4)	
O4	0.0392(11)	0.8217(10)	0.5362(9)	0.057(3)	
O5	– 0.1569(10)	0.5992(8)	0.9893(7)	0.042(3)	
O6	0.0909(9)	0.5331(9)	0.8110(8)	0.043(3)	
O7	– 0.1271(11)	0.7579(8)	0.7355(8)	0.048(3)	
O8	– 0.1814(9)	0.5035(8)	0.8006(8)	0.036(2)	
O9	– 0.1928(9)	0.7768(9)	0.5474(8)	0.045(3)	
O10	– 0.3419(12)	0.9707(8)	0.3448(9)	0.054(3)	
O11	– 0.5024(13)	0.8579(12)	0.6154(10)	0.081(4)	
O12	– 0.4091(10)	0.7194(8)	0.4621(9)	0.051(3)	
O13	– 0.6346(10)	0.8278(8)	0.8210(7)	0.039(3)	
O14	– 0.7436(10)	0.5947(8)	0.8841(9)	0.048(3)	
O15	– 0.4216(10)	0.5938(9)	0.8630(10)	0.053(3)	
O16	– 0.6344(10)	0.6300(8)	1.0660(8)	0.043(3)	
O17	– 0.4692(14)	0.3307(9)	0.6577(9)	0.074(4)	
O18	– 0.6684(10)	0.4180(8)	0.8276(8)	0.037(3)	
O19	– 0.6060(9)	0.5942(8)	0.5629(8)	0.039(3)	
O20	– 0.3737(10)	0.4928(10)	0.7188(8)	0.053(3)	
O1W[a]	– 0.3851(137)	0.9319(122)	1.0064(126)	0.520(80)	0.50
N1	– 0.0045(14)	0.4158(10)	0.6219(10)	0.214(14)	
C2	– 0.0727(13)	0.4004(9)	0.5392(11)	0.155(9)	
C3	– 0.1214(11)	0.5224(12)	0.4469(13)	0.143(9)	
C4	0.0420(30)	0.2921(16)	0.7117(20)	0.164(26)	0.50
N11[b]	– 0.2357(20)	0.9348(20)	0.9419(34)	0.345(30)	0.50
C12[b]	– 0.3130(21)	0.8888(24)	0.8869(35)	0.281(30)	0.50
C13[b]	– 0.4663(21)	0.9000(20)	0.9468(42)	0.316(32)	0.50
N14[b]	– 0.5191(23)	1.0331(18)	0.9038(36)	0.353(31)	0.50
C15[b]	– 0.4399(24)	1.0838(24)	0.9530(39)	0.329(33)	0.50
C16[b]	– 0.2860(22)	1.0685(18)	0.8965(44)	0.372(33)	0.50
C17[b]	– 0.0802(21)	0.9172(39)	0.8914(55)	0.224(34)	0.50

[a] According to the TG analysis two water molecules per unit cell are expected. From structure analysis only one molecule has been located. [b] Disordered organic species.

Table 4. Selected bond lengths for the cobaltgallophosphate IM-6 (sample A).[a]

M(1)−O(1)	1.842(11)	M(2)−O(5)	1.847(10)
M(1)−O(2)	1.835(10)	M(2)−O(6)	1.843(10)
M(1)−O(3)	1.850(11)	M(2)−O(7)	1.824(10)
M(1)−O(4)	1.837(11)	M(2)−O(8)	1.866(10)
M(3)−O(9)	1.871(10)	M(4)−O(13)	1.858(10)
M(3)−O(10)	1.871(11)	M(4)−O(14)	1.839(10)
M(3)−O(11)	1.810(12)	M(4)−O(15)	1.859(11)
M(3)−O(12)	1.855(12)	M(4)−O(16)	1.870(11)
M(5)−O(17)	1.821(11)	P(1)−O(3)	1.485(11)
M(5)−O(18)	1.844(10)	P(1)−O(4)	1.526(11)
M(5)−O(19)	1.863(10)	P(1)−O(7)	1.525(10)
M(5)−O(20)	1.823(11)	P(1)−O(9)	1.538(10)
P(2)−O(2)	1.510(11)	P(3)−O(8)	1.523(10)
P(2)−O(10)	1.498(11)	P(3)−O(15)	1.508(12)
P(2)−O(11)	1.497(12)	P(3)−O(16)	1.523(10)
P(2)−O(13)	1.542(10)	P(3)−O(20)	1.513(11)
P(4)−O(1)	1.509(11)	P(5)−O(5)	1.525(10)
P(4)−O(12)	1.510(11)	P(5)−O(6)	1.523(10)
P(4)−O(17)	1.525(12)	P(5)−O(14)	1.497(11)
P(4)−O(19)	1.510(10)	P(5)−O(18)	1.519(10)
N(1)−C(2)	1.479(10)	N(11)−C(12)	1.50(2)[b]
N(1)−C(3)	1.475(10)	N(11)−C(16)	1.50(2)[b]
N(1)−C(4)	1.498(10)	N(11)−C(17)	1.50(2)[b]
C(2)−C(3)	1.503(10)	N(14)−C(13)	1.50(2)[b]
		N(14)−C(15)	1.50(2)[b]
		C(12)−C(13)	1.50(2)[b]
		C(15)−C(16)	1.50(2)[b]

[a] M corresponds to gallium and cobalt atoms. [b] For the disordered amine, the N−C and C−C bond lengths were fixed to 1.50(2) Å.

Table 5. Selected angles of the cobaltgallophosphate IM-6 (Sample A).[a]

O(1)-M(1)-O(2)	114.8(5)	O(5)-M(2)-O(6)	112.8(4)
O(1)-M(1)-O(3)	103.7(5)	O(5)-M(2)-O(7)	103.9(5)
O(1)-M(1)-O(4)	106.1(5)	O(5)-M(2)-O(8)	117.9(4)
O(2)-M(1)-O(3)	108.7(5)	O(6)-M(2)-O(7)	111.3(5)
O(2)-M(1)-O(4)	113.9(5)	O(6)-M(2)-O(8)	99.8(5)
O(3)-M(1)-O(4)	109.1(6)	O(7)-M(2)-O(8)	111.3(5)
O(9)-M(3)-O(10)	109.0(5)	O(13)-M(4)-O(14)	110.4(5)
O(9)-M(3)-O(11)	108.7(5)	O(13)-M(4)-O(15)	111.6(5)
O(9)-M(3)-O(12)	105.9(5)	O(13)-M(4)-O(16)	105.6(4)
O(10)-M(3)-O(11)	118.7(6)	O(14)-M(4)-O(15)	114.4(5)
O(10)-M(3)-O(12)	105.4(5)	O(14)-M(4)-O(16)	108.4(5)
O(11)-M(3)-O(12)	108.4(6)	O(15)-M(4)-O(16)	106.0(5)
O(17)-M(5)-O(18)	104.8(5)	O(3)-P(1)-O(4)	114.2(7)
O(17)-M(5)-O(19)	111.3(5)	O(3)-P(1)-O(7)	104.6(6)
O(17)-M(5)-O(20)	104.1(6)	O(3)-P(1)-O(9)	112.0(7)
O(18)-M(5)-O(19)	111.1(5)	O(4)-P(1)-O(7)	110.4(6)
O(18)-M(5)-O(20)	111.8(5)	O(4)-P(1)-O(9)	105.3(6)
O(19)-M(5)-O(20)	113.3(5)	O(7)-P(1)-O(9)	110.5(6)
O(2)-P(2)-O(10)	109.7(6)	O(8)-P(3)-O(15)	107.7(6)
O(2)-P(2)-O(11)	110.1(7)	O(8)-P(3)-O(16)	109.9(6)
O(2)-P(2)-O(13)	108.6(6)	O(8)-P(3)-O(20)	106.9(6)
O(10)-P(2)-O(11)	111.7(7)	O(15)-P(3)-O(16)	110.2(6)
O(10)-P(2)-O(13)	107.7(6)	O(15)-P(3)-O(20)	113.8(6)
O(11)-P(2)-O(13)	109.0(6)	O(16)-P(3)-O(20)	108.2(6)
O(1)-P(4)-O(12)	109.4(6)	O(5)-P(5)-O(6)	108.5(6)
O(1)-P(4)-O(17)	107.2(6)	O(5)-P(5)-O(14)	111.2(6)
O(1)-P(4)-O(19)	109.3(6)	O(5)-P(5)-O(18)	106.6(6)
O(12)-P(4)-O(17)	111.3(7)	O(6)-P(5)-O(14)	110.2(6)
O(12)-P(4)-O(19)	111.0(6)	O(6)-P(5)-O(18)	108.3(6)
O(17)-P(4)-O(19)	108.6(6)	O(14)-P(5)-O(18)	111.9(6)

[a] M corresponds to gallium and cobalt atoms.

To compensate the negative charge of the inorganic framework, organic species are occluded in their protonated forms. XRD analysis on the sample calcined at 600 °C under air shows a collapsing of the IM-6 structure.

Structure description: Five distinct crystallographic sites are observed for P and for (Ga + Co) atoms. The TO_4 tetrahedra (T = Ga, Co or P) are quite regular and the T−O bond lengths correspond to those usually found in other gallophosphates ($1.48(1) < d(\text{P–O}) < 1.52(1)$ Å) and ($1.81(1) < d(\text{Ga–O})$ or $d(\text{Co–O}) < 1.87(1)$ Å). No distinction between cobalt and gallium atoms can be predicted as the Co–O and Ga–O bond lengths are similar.

The three-dimensional framework of IM-6 is exclusively built from TO_4 tetrahedra. This new framework topology displays two types of interconnected channels : the first one, delimited by ten-membered rings, runs along the $[0\bar{1}1]$ direction, whereas the other, parallel to the [100] direction, is delimited by twelve-membered rings (see Figures 5 and 6, respectively). The network is composed of four-, six-, ten-, and twelve-membered rings. It is worth noting that the projection of the structure along the [100] direction shows the same 4 × 6 × 12 ring arrangement (see Figure 6) as previously observed, for example, in the AFI[17] and BOG[18] structure types. However, the shape of the ten-membered-ring channel differs completely from those of boggsite.

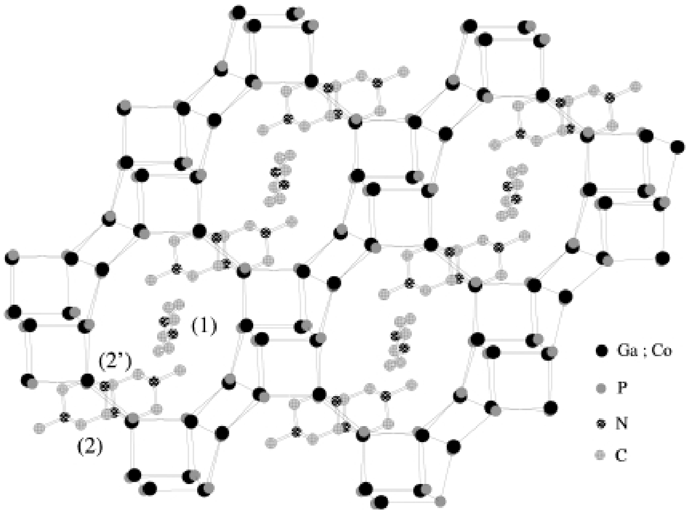

Figure 5. View along $[0\bar{1}1]$ direction showing the ten-membered-ring channels and the two nonequivalent amines. The occupancy factors of the amines (2) and (2′) and of the methyl groups of amine (1) are equal to 0.5. Framework oxygen atoms and water molecule are omitted for clarity.

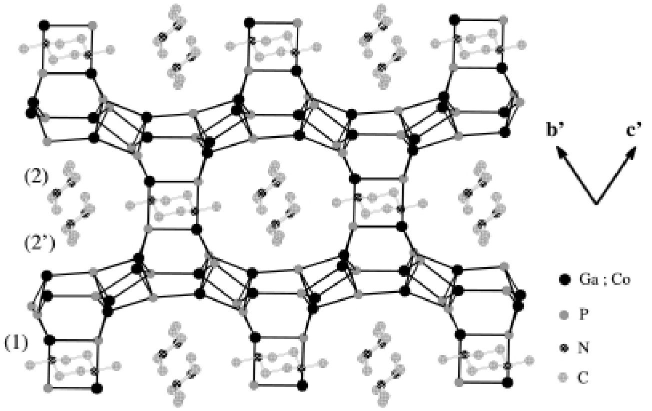

Figure 6. Projection of the structure of IM-6 along [100] direction showing the 4 × 6 × 12 ring connections leading to the twelve-membered-ring channels. The occupancy factors of the amines (2) and (2′) and of the methyl groups of amine (1) are equal to 0.5. Framework oxygen atoms and water molecule are omitted for clarity. $c' = c \times \cos(90-\beta)$; $b' = b \times \cos(90-\gamma)$.

The structure can also be described as layers built from chains of four- and six-membered rings running along the [100] direction. Each layer is connected to each other through a single four-membered-ring unit leading to the 3D framework (see Figure 7).

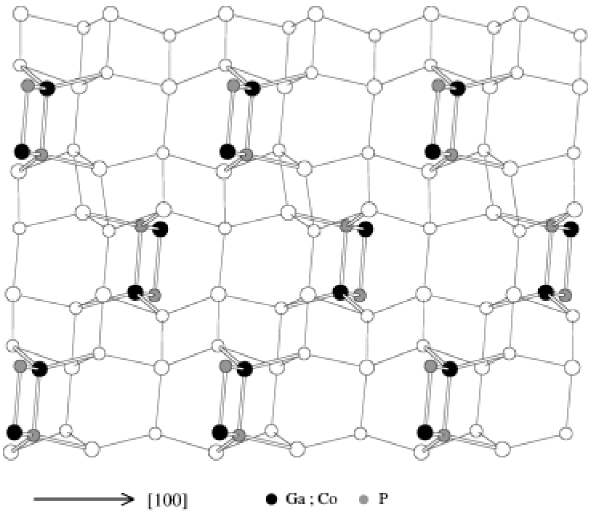

Figure 7. View of chains of four- and six-membered rings running along the [100] direction, and the four-membered ring connectivity units (thick lines, and black (Ga) and grey (P) atoms)

Two distinct organic species are present in the two-dimensional channel system. These molecules are not located at the intersection of the channel system, but are preferentially trapped in the ten- and twelve-membered-ring windows where hydrogen interactions could be stronger (see Figures 6 and 7). The amines are therefore in strong interaction through hydrogen bonding with the inorganic framework. For example, an hydrogen bond length $d(N1 \cdots O8) = 2.91$ Å can be found for the amine located in the ten-membered-ring windows.

Conclusion

IM-6 was obtained in the presence of N-substituted piperazines as the organic template under solvothermal conditions. The structure of this new cobaltgallophosphate is purely composed of PO_4, GaO_4, and CoO_4 tetrahedra and represents a new framework topology. The inorganic framework is fully connected (no P–OH groups) and displays a two-dimensional channel system with ten- and twelve-membered-ring apertures. This solid is obtained in the presence of various organic species from the piperazine family. It is worth noting that silicon can be homogenously introduced in the inorganic framework leading to a CoGaPSO material.

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