

## Synthesis and Characterisation of the first Three-dimensional Framework Cobalt–Gallium Phosphate $[\text{C}_5\text{H}_5\text{NH}]^+[\text{CoGa}_2\text{P}_3\text{O}_{12}]^-$

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The synthesis and characterisation of the first heteroatom-substituted gallium phosphate are described; the three-dimensional structure is unique and contains large pores in which pyridinium cations reside.

In the quest for new microporous zeolitic materials, there has recently been much interest in the synthesis of open-framework metal phosphates, in particular those of aluminium,<sup>1</sup> and gallium.<sup>2</sup> There has also been much research into the incorporation of heteroatoms into such existing frameworks to modify their physical and chemical properties. Thus replacement of either P or Al in AlPOs by species of lower valency *e.g.* Si for P to give SAPOs or  $\text{M}^{2+}$  for Al to give MAPOs ( $\text{M} = \text{Mg}, \text{Zn}$  and most first-row transition metals) can lead to novel solid acids with enhanced catalytic properties. For example, CrAPO-5 has been found to be effective as a catalyst for the oxidation of secondary alcohols<sup>3</sup> and SAPO-34 catalyses the conversion of methanol to olefins.<sup>4</sup>

Gallium phosphates show a similar structural diversity to AlPOs. A number of GaPOs have isostructural AlPO analogues *e.g.*  $\text{GaPO}_4 \cdot 12(\text{en})$ <sup>5</sup> and  $\text{GaPO}_4 \cdot 21$ ,<sup>6</sup> whilst some, such as cloverite,<sup>7</sup> are unique. Although several fluorinated GaPOs have been reported,<sup>8–10</sup> to our knowledge, there have been no reports to date of syntheses of gallium phosphates with metal-substituted frameworks. Here, we report the synthesis and characterisation of the first open framework cobalt-gallium phosphate.

The compound was synthesised under hydrothermal conditions from a predominantly nonaqueous system. 0.5 g  $\text{Ga}_2\text{O}_3$  and 0.8 g CoO were dispersed in 7.8  $\text{cm}^3$  of butan-1-ol by stirring and 0.1  $\text{cm}^3$  of  $\text{Si}(\text{OEt})_4$  added to act as a mineraliser. After further stirring, 1  $\text{cm}^3$  of orthophosphoric acid was added to give a gel of overall composition  $\text{Ga}_2\text{O}_3 \cdot 4\text{CoO} \cdot 3.8\text{H}_3\text{PO}_4 \cdot 32\text{BuOH} \cdot 0.1\text{Si}(\text{OEt})_4 \cdot 9.3\text{py}$ . The gel was sealed in a Teflon-lined stainless-steel autoclave and heated at 180 °C for 7 days. The solid product was collected by filtration, washed with distilled water and dried overnight at 80 °C. Examination

under the optical microscope revealed three distinct crystalline components including deep-blue flakes of the compound of interest and pale pink plates subsequently shown to be a second cobalt gallium phosphate of composition  $\text{NH}_4[\text{CoGa}_2\text{P}_3\text{O}_{12}(\text{H}_2\text{O})_2]$  (monoclinic, space group  $C2/c$ ,  $a = 13.314$ ,  $b = 10.243$ ,  $c = 8.885$  Å,  $\beta = 108.43^\circ$ ).<sup>11</sup> The majority of the product was white polycrystalline material, identified by powder X-ray diffraction as the  $\alpha$ -quartz analogue of  $\text{GaPO}_4$  (hexagonal;  $a = 4.90$ ,  $c = 11.05$  Å).<sup>12</sup> Analytical electron microscopy of a finely ground sample of the blue crystals selected from the product mixture showed no silicon present. All the crystallites analysed contained Ga, Co and P and the total metal concentration was equal to that of phosphorus, *i.e.*  $(\text{Ga} + \text{Co}) : \text{P}$  was always 1 : 1. The general formula of the framework can therefore be written as  $\text{Co}_x\text{Ga}_{(1-x)}\text{PO}_y$  ( $0.23 \leq x \leq 0.63$ ) (the oxygen content cannot be determined from electron microscopy measurements). The majority of the crystallites however had Ga : Co present in the ratio 2 : 1. A crystal was selected for study by four-circle diffractometry.<sup>†</sup>

The structure consists of almost regular  $\text{MO}_4$  ( $\text{M} = \text{Co}$  or  $\text{Ga}$ ) and  $\text{PO}_4$  tetrahedra with fully shared vertices ( $\text{M}-\text{O}_{\text{av}} 1.85$  Å,  $\text{O}-\text{M}-\text{O}_{\text{av}} 109.5^\circ$ ,  $\text{P}-\text{O}_{\text{av}} 1.52$  Å,  $\text{O}-\text{P}-\text{O}_{\text{av}} 109.5^\circ$ ). The M–O and P–O bond lengths are comparable to those seen in other GaPOs.<sup>5,6</sup> The presence of  $\text{Co}^{\text{II}}$  in tetrahedral sites explains the blue colour of the crystals as has been observed previously for DAF-2,  $\text{CoPO}_4 \cdot 0.5(\text{en})$ .<sup>15</sup> The tetrahedral units are linked in an alternating manner to give an open three-

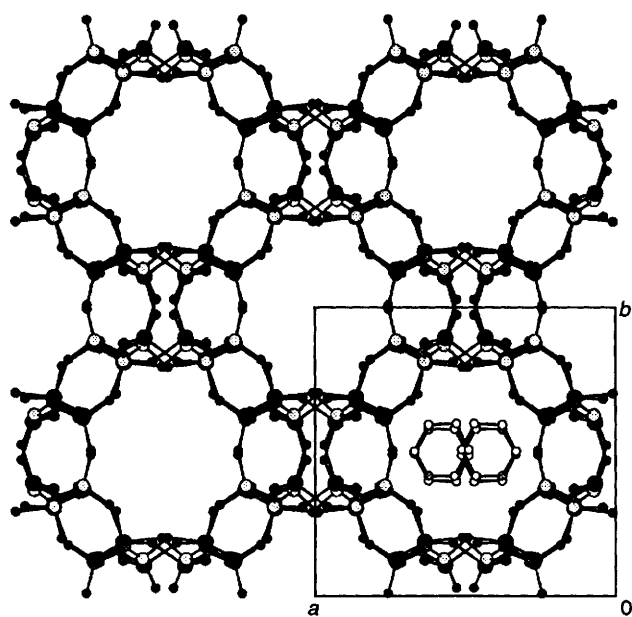


Fig. 1 View of title compound along  $c$  axis. Pyridinium cations are shown stacked in one of the tunnels constructed from puckered ten-membered rings (key for framework is as for Fig. 2, N is shaded and C unshaded in the pyridinium cations).

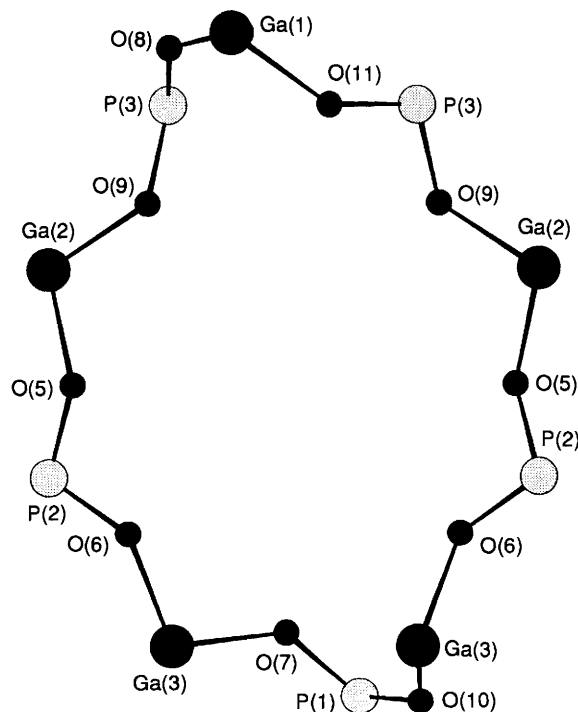


Fig. 2 Puckered ten-membered ring generated from alternation  $\text{PO}_4$  and  $(\text{Ga}, \text{Co})\text{O}_4$  tetrahedra. (N.B. Sites labelled Ga actually have site occupancy  $\text{Ga}_{2/3}\text{Co}_{1/3}$ ). Selected  $\text{O} \cdots \text{O}$  distances are:  $\text{O}(5) \cdots \text{O}(5)$  6.90,  $\text{O}(5) \cdots \text{O}(6)$  6.52,  $\text{O}(5) \cdots \text{O}(9)$  6.39,  $\text{O}(6) \cdots \text{O}(6)$  5.32,  $\text{O}(6) \cdots \text{O}(9)$  7.09,  $\text{O}(7) \cdots \text{O}(9)$  6.55,  $\text{O}(7) \cdots \text{O}(9')$  7.31,  $\text{O}(7) \cdots \text{O}(11)$  8.68,  $\text{O}(8) \cdots \text{O}(10)$  10.69,  $\text{O}(9) \cdots \text{O}(9)$  4.63 Å.

dimensional framework of  $[\text{CoGa}_2\text{P}_3\text{O}_{12}]^-$  consisting of four-, six- and ten-membered rings (Fig. 1). The most interesting features are the channels running parallel to the  $c$  axis which have puckered windows containing 10 T atoms (T = Ga, Co and P) with a range of O...O distances up to 10.68 Å (Fig. 2). The charge compensating pyridinium cations lie in these channels and interact only weakly with the framework (shortest N...O distance 3.3 Å) suggesting the possibility of relatively easy removal in order to exploit the microporous nature of the material. This is currently being investigated.

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### Footnote

† A crystal suitable for X-ray analysis (size  $0.1 \times 0.35 \times 0.2$  mm) was obtained from the synthesised material. Crystal data for  $\text{C}_5\text{H}_6\text{CoGa}_2\text{NO}_{12}\text{P}_3$ ,  $M = 563.40$ , monoclinic, space group  $C2/c$ ,  $a = 15.058(2)$ ,  $b = 13.197(3)$ ,  $c = 15.273(5)$  Å,  $\beta = 112.20(9)^\circ$ ,  $V = 2810.04$  Å<sup>3</sup>,  $Z = 8$ ,  $\mu(\text{Cu-K}\alpha) = 180.84$  cm<sup>-1</sup>,  $D_c = 2.66$  g cm<sup>-3</sup>. Data were collected on an Enraf-Nonius CAD4 diffractometer using the  $\omega$ - $2\theta$  technique, for the range  $0 < 2\theta < 144^\circ$ . The total number of reflections measured was 6960, of which 2754 were unique and 1704 had  $I > 3\sigma(I)$ . The structure was solved by direct methods (SHELX-86).<sup>13</sup> All non-hydrogen atoms were located easily in Fourier maps and the occupancy of each of the three metal sites was set to 1/3 Co and 2/3 Ga to balance the charge of the pyridinium cations and to satisfy the framework stoichiometry deduced from analytical electron microscopy results. Hydrogen atoms on the

template molecules were placed geometrically. Refinement of 218 variables was by full-matrix least squares (CRYSTALS).<sup>14</sup> The final residual were  $R = 0.052$  and  $R_w = 0.065$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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