Synthesis and characterisation of $[C_4NH_{10}]^+[CoGaP_2O_8]^-$, a CoGaPO analogue of the zeolite gismondine

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The synthesis and characterisation of a new templated cobalt–gallium phosphate, which is isostructural with the zeolite gismondine and the substituted aluminium phosphates MAPO-43 and SAPO-43, is described.

There has recently been much interest in the synthesis of novel microporous metal phosphates, in particular those of aluminium and gallium. Incorporation of heteroatoms into the frameworks of aluminium phosphates has been shown to lead to materials with potentially useful catalytic and ion-exchange properties. For example, the cobalt–aluminium phosphate CoAPO-18[1] catalyses the conversion of methanol into light hydrocarbons and CrAPO-5[2] is an effective catalyst for the oxidation of secondary alcohols.

A large number of microporous gallium phosphates are known, but no metal-substituted gallium phosphates had been reported until recently when we described the synthesis and structural characterisation of $[C_5NH_6]^+[CoGa_2P_3O_{12}]^-$[3]. Here we report the synthesis of a novel cobalt–gallium phosphate, in which the framework has an intersecting network of channels of similar size to those present in zeo- lites of commercial importance and is isostructural with the naturally occurring zeolite gismondine[4] and the synthetic materials gismondine-type P zeolite,[5] SAPO-43[6] and MAPO-43.[7]

The compound was synthesised under solvothermal conditions from a predominantly non-aqueous system. 0.4 g each of finely ground CoO and Ga_2O_3 were dispersed in 6 cm^3 ethylene glycol by vigorous stirring. 2 cm^3 of pyrrolidine was added to act as template and 0.1 cm^3 of $Si(OEt)_4$ to improve the crystallinity of the product.[8] The mixture was stirred for 5 min, then 1.5 cm^3 of aqueous H_3PO_4 (85% by mass) was added to give a gel of overall composition Ga_2O_3 : 2.5 CoO : 10 H_3PO_4 : 42 HOC_2H_4OH : 0.30 $Si(OEt)_4$: 5.6 C_4NH_9. This was stirred until homogeneous and sealed in a Teflon-lined stainless-steel autoclave. After heating for 7 days at 180 °C, the product was collected by filtration, washed with distilled water and dried in air at 80 °C for 24 hours. Examination under an optical microscope showed the product to consist solely of deep-blue octahedral crystals. A single crystal was selected suitable for study by X-ray diffractometry.†

Energy dispersive X-ray analysis using an electron microscope showed that the compound contained Co, Ga and P in approximately constant proportions, but no silicon could be detected. Analysis of 25 crystallites showed the overall metal : P ratio to vary between 0.925 and 1.224, while the Ga : Co ratio varied from 0.802 to 1.312. Overall, metal : P = 1.00(8) and Ga : Co = 1.06(11), corresponding to a framework composition $Co_{0.97}Ga_{1.03}P_2O_x$ (the oxygen content cannot be determined by analytical electron microscopy). A powder X-ray diffraction pattern further confirmed that the product was monophasic.

Combustion analysis showed the material to contain 3.44% N, 11.60% C and 2.42% H by mass. This is in reasonable agreement with the idealised formula $[C_4NH_{10}]^+[CoGaP_2O_8]^-$ (N 3.58%, C 12.30% and H 2.58%).

Thermogravimetric analysis (N_2 atmosphere, heating rate 10 °C min^{-1}) shows that a gradual loss of mass occurs over the temperature range 10–400 °C, and a sharper loss of mass in the range 400–600 °C, giving a total loss of mass of 12.2%. The residue is a solid black material, which is shown by powder X-ray diffraction to be amorphous. A further loss of mass occurs at temperatures above 800 °C, possibly due to loss of P_4O_{10}.

The structure consists of MO_4 (M = Co, Ga) and PO_4 tetrahedra with almost regular geometry (M–O_{av} 1.860 Å, O–M–O_{av} 109.3°, P–O_{av} 1.511 Å, O–P–O_{av} 109.2°). These are linked through all vertices to form an open three-dimensional anionic framework with composition $[CoGaP_2O_8]^-$. Cavities

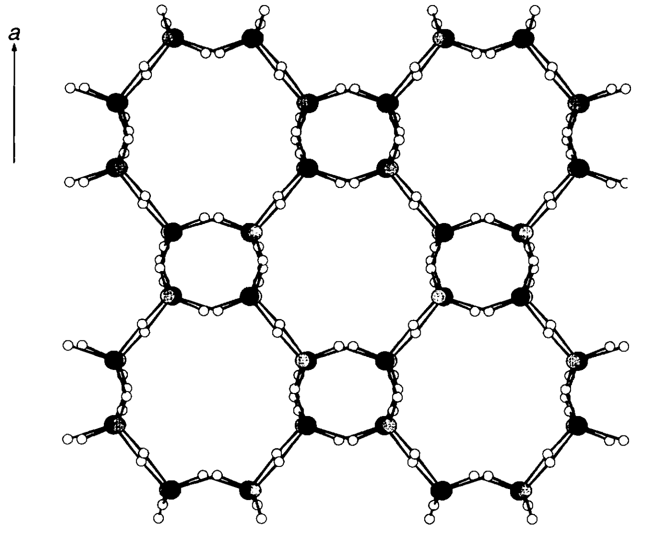

Fig. 1 View of $[C_4NH_{10}]^+[CoGaP_2O_8]^-$ along the vector [0, 1, 1] showing one of the two symmetry-related sets of channels. Template molecules have been omitted for clarity. Key: metal sites black, P grey, O white.

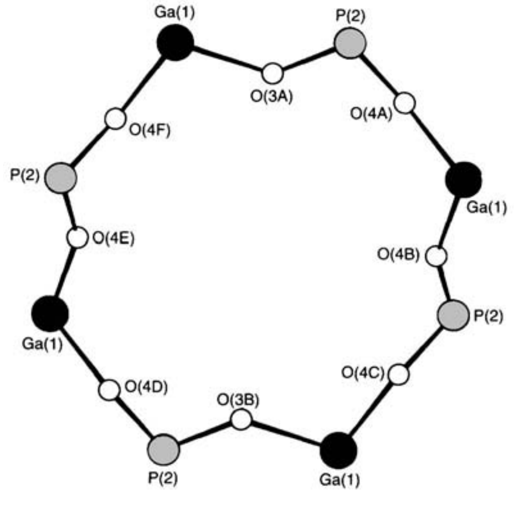

Fig. 2 View of eight-membered ring bounding one of the channels. Atom shading and orientation as in Fig. 1. Sites labelled Ga have site occupancy $Ga_{0.5}Co_{0.5}$. Selected O···O distances (Å) are: O(3A)···O(3B) 6.59, O(4A)···O(4D) 7.66, O(4B)···O(4E) 6.50, O(4C)···O(4D) 7.03.

within this framework contain the $C_4NH_{10}^+$ cations, which are disordered over four symmetry-related positions. The cavities are linked to form a three-dimensional network of channels running parallel to the vectors [0,1,1] and [0,1,−1] (Fig. 1). These channels have diameters of *ca.* 6.5 Å (Fig. 2). The framework is isostructual with that of the naturally occurring zeolite mineral gismondine, $Ca_4[Al_8Si_8O_{16}]$, which has smaller channels with diameters *ca.* 4.5 × 4.8 Å.[4] Synthetic polytypes are also known, including the silicon aluminium phosphate SAPO-43 (6.166 × 6.851 Å) and the magnesium aluminium phosphate MAPO-43 (6.752 × 6.348 Å). The pore size of the material is comparable to that present in zeolites of commercial importance such as ZSM-5[11] $\{Na_n\text{-}\ [Al_nSi_{96-n}O_{192}]$, channel diameter *ca.* 5.5 Å$\}$.

A. M. C. thanks the University of Oxford for a Glasstone Research Fellowship and A. R. C. thanks the EPSRC for a studentship.

Footnote

† A crystal suitable for X-ray analysis (size 0.2 × 0.3 × 0.3 mm) was selected from the synthesised material. *Crystal data* for $CoGaP_2O_8C_4NH_{10}$: M = 390.73, orthorhombic, space group *Fddd*, a = 10.0033(5), b = 14.500(3), c = 15.066(2) Å, U = 2185.5 Å^3, Z = 8, μ(Mo-Kα) = 47.91 cm^{-1}, D_c = 2.38 g cm^{-3}. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using the ω–2θ technique for the range $0 < 2\theta < 60°$. The total number of reflections measured was 4654 of which 809 were unique and 692 had $I > 2\sigma(I)$. The structure was solved by Patterson methods (SHELX-86).[9] All framework atoms were located in observed Fourier maps and the occupancy of the metal site was set to 0.5 Co, 0.5 Ga to satisfy the framework stoichiometry. The template was modelled as disordered over four symmetry-equivalent sites. One template atom is 2.91 Å from O(12), indicative of hydrogen bonding; this site was therefore assigned as nitrogen. Template hydrogen atoms were positioned geometrically. Refinement of 53 variables was by full-matrix least squares (CRYSTALS).[10] The final residuals were R = 0.0319 and R_w = 0.0380. 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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Received, 11th December 1995; Com. 5/08041J