The Synthesis and Crystal Structure of a Novel Clay-like Gallophosphate with Sub-unit-cell Intergrowths of Ethylenediamine: $[GaPO_4(OH)]^- \ 0{\cdot}5(H_3NCH_2CH_2NH_3)^{2+}$

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The preparation and crystal structure of the title compound in which the Ga is octahedrally and the P is tetrahedrally coordinated is described: the structure is the first fully characterised example of a layered gallophosphate.

Catalysts and adsorbents that are derived from naturally occurring aluminosilicate minerals *e.g.* zeolites and clays have proved useful in a wide variety of contexts.[1–5] In the case of montmorillonites and vermiculites considerable scope exists for the engineering of new materials possessing unusual catalytic, optical or other properties.[6–9] Of late, several other layered inorganic solids, especially the phosphates of zirconium have been effectively exploited as sensors, ion-exchangers, solid electrolytes and catalysts.[10] All layered solids are, in principle, amenable to isomorphous substitution so as to modify the layer charge and thereby influence the resulting solids aptitude to incorporate organic guest species in the interlamellar regions.[11,12] In this communication we describe the three-dimensional structure of a novel gallophosphate, the unit cell and space group of which have been previously reported.[13] This has a structural kinship with the simplest of the layered aluminosilicates and with the organic intercalates that they form.[14]

We have recently characterized one-,[15] two-[16,17] and three-[18]dimensionally continuous structures of aluminium phosphates. There is at least equal interest in synthesizing open structures of gallium phosphate, since they are known[19] to be potentially capable of crystallizing as three-dimensionally microporous materials containing large apertures.

Single crystals† of the title compound were obtained, together with other unidentified phases, from a route involving the use of ethyleneglycol as the solvent. In a typical synthesis a mixture of GaOOH, phosphoric acid (85%), ethylenediamine and ethyleneglycol with a composition of $Ga_2O_3 : 2.0P_2O_5 : 10C_2N_2H_8 : 44.2C_2H_6O_2 : 6.0H_2O$ was sealed in a Teflon-lined autoclave and heated at 180 °C for 25 days under autogeneous pressure. The product was filtered off, washed with water and dried at ambient temperature. By using water as the reaction medium, monophasic powder of the title compound could be synthesized in a way similar to that described in the literature.[13] In this case, the typical composition of the reaction mixture was $Ga_2O_3 : 1.5P_2O_5 : 1.5C_2N_2H_8 : 60H_2O$.

Interatomic contacts in the structure of the layered gallophosphate (see Fig. 1) fall in the range previously found in three-dimensional gallophosphates.[23] Bond valence calculations[24] indicate that one of the oxygen atoms O(1) is from a hydroxy group, and is part of a Ga–(OH)–Ga moiety. One of the oxygen atoms [O(3)] triply bridges two galliums and a phosphorus atom. The structure consists of macroanionic sheets normal to [001] having a formula $[GaPO_4(OH)]^-$, in which the Ga atoms are in the centre of the sheet and are flanked by PO_4 tetrahedra. Within a sheet each gallium atom is coordinated by six oxygen atoms to form a slightly distorted octahedron. If an equatorial plane is considered to consist of O(1) and O(3), and their centrosymetrically related atoms, it is seen that edge sharing chains of GaO_6 run parallel to [010]. Adjacent gallium atoms within a chain are spanned by two oxygen atoms of PO_4 unit in a regular, alternating manner. The chains are then cross linked *via* the triply bridging oxygen atom O(3) giving rise to the sheets.

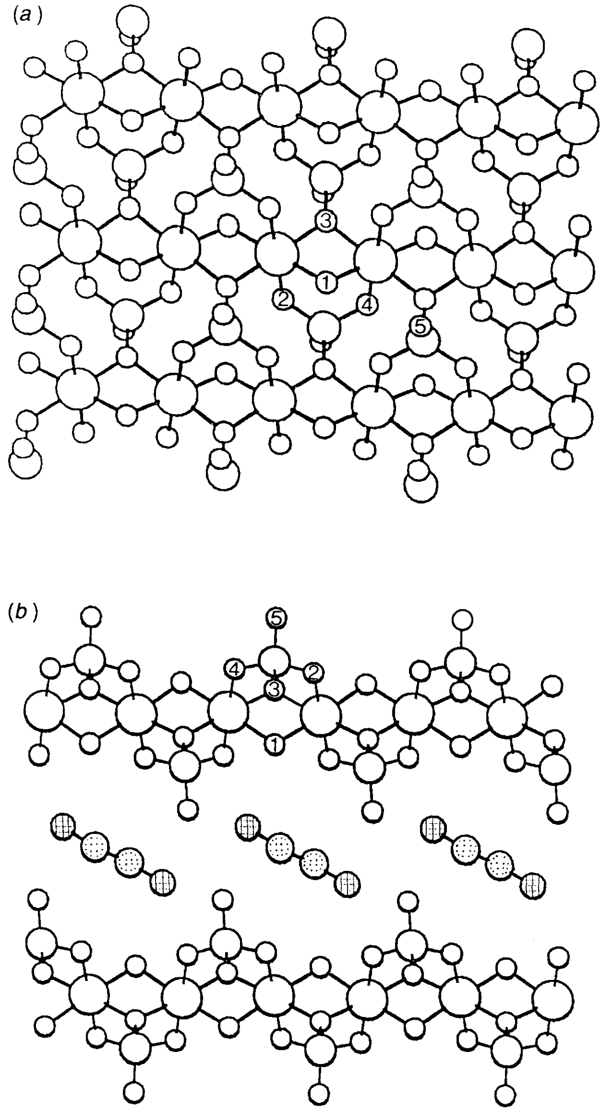

Fig. 1 The recently characterized gallophosphate sheet structure. (*a*) The view normal to the plane of the sheet. (*b*) The view along the sheet plane (interlamellar layer retained). Selected ranges and interatomic contacts (Å) and angles (°) Ga–O 1.939 to 2.004; P–O 1.504 to 1.585; N–O(2) 2.82; N–O(5) 2.75 to 2.76; O–Ga–O 176.8 to 178.8 (*trans*); O–Ga–O 80.0–101.6 (*cis*); O–P–O 106.4 to 112.1; Ga–O–Ga 97.1 to 100.4; Ga–O–P 125.8 to 131.5. Large circles, Ga; intermediate circles, P; small circles, O; speckled circles, C; hatched circles, N.

Charge-balancing ethylenediammonium cations are located between the layers and are hydrogen-bonded to terminal P–O groups. The bond length of a terminal group 1.504(8) Å indicates that there is substantial multiple bond character in this functionality and is comparable to those found in terminal P=O groups found in $H_3PO_4{\cdot}0.5H_2O$ (1.485 and 1.497 Å).[25] We see no evidence for the presence of P–OH groups since the terminal P=O group is much shorter than the P–OH groups found in $H_3PO_4{\cdot}0.5H_2O$ (avg. 1.551 Å)[25] and α-zirconiumphosphate (avg. 1.558 Å).[26] The terminal P=O groups are located on the outer faces of the sheets unlike those found in the naturally occurring clay minerals[14] where analogous linkages are directed towards the centre of the sheet. In this respect the gallophosphate is similar to α-zirconiumphosphate in that the terminal P–O groups are directed towards the interlamellar region.

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† *Crystal data* for $[GaPO_4(OH)]^-$ $0.5(C_2N_2H_{10})^{2+}$: M_r = 212.76 monoclinic, space group = $P2_1/c$ a = 4.4643(9), b = 5.994(1), c = 18.538(2) Å, β = 94.71(1)°, V = 494.4 Å^3, D_c = 2.858 g cm^{-3}, Z = 4, μ(Mo-Kα) = 58.07 cm^{-1}. X-Ray measurements were made using an Enraf-Nonius FAST TV, area detector and graphite monochromated Mo-Kα radiation. Intensity data corresponding to one hemisphere of reciprocal space were recorded using two ω scan ranges of 100° with a φ shift of 90° (to achieve >180° in total) at χ = 0°, followed by two further ω rotations of 70° with a φ shift of 90° at χ = 90°, to record the missing cusp data, with a swing angle of 18.0° and a crystal to detector distance of 45.6 mm which yielded all possible reflections to θ_{max} of 22.4°. Of the reflections predicted and scanned, 1309 satisfied the conditions for acceptable measurement and were merged to give 608 unique data of which 569 were considered to be observed ($F_o > 3\sigma F_o$) and corrected for absorption.[20] The structure was solved by direct methods,[21] and refined by full-matrix least-squares analysis[22] to R = 0.043, R_w = 0.046. Organic H atoms were located in difference Fourier maps and refined with restraints being applied to maintain C–H and N–H geometry. Anisotropic thermal parameters were employed for the Ga and P atoms with isotropic thermal parameters for the remaining atoms (one equivalent temperature parameter for the H Atoms), total of 63 parameters were used. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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