

Synthesis and crystal structure of $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$; a new structure-type for layered acid phosphates†

Steven K. Rishi,^a Benson M. Kariuki,^a Neal J. Checker,^a John Godber^b and Adrian J. Wright^{*a}

Received (in Cambridge, UK) 7th October 2005, Accepted 2nd December 2005

First published as an Advance Article on the web 5th January 2006

DOI: 10.1039/b514246f

The crystal structure of the layered acid phosphate, $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, has been determined and provides a new structure-type for a series of metal phosphates with interlamellar regions likely to be highly suited to intercalation behaviour.

Low-dimensional materials composed of layers of strongly bound species, held together by relatively weak bonding between layers, as exemplified by the sheet-like structures of the phyllosilicates, have received significant attention due to the extensive chemical manipulations that are possible within the interlamellar region. The diversity of this chemistry is partly a consequence of variations in the inherent layer charges; phyllosilicates have predominantly negatively charged layers, layered double hydroxides positively charged layers and the metal phosphates and phosphonates neutral layers. These materials can provide numerous desirable properties, including ion exchange, ionic conductivity and intercalation with potential to many applications.¹ Furthermore, much interest has recently centred on the exfoliation of these materials into discrete nano-dimensional lamellae which have found application in polymer-based nanocomposites² and self-assembled multilayers.³

The most studied of the layered phosphates are the zirconium phosphates, $\alpha\text{-Zr}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$ and $\gamma\text{-Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$, which have structures consisting of zirconium phosphate layers with exchangeable protons protruding into the inter-layer region and have been shown to exhibit proton conductivity, and facilitate intercalation, exfoliation and catalysis.⁴ These structural features are clearly advantageous but are relatively rare and therefore we have initiated a search for more examples. We are particularly interested in isolating such structures where transition metal ions are included, which may provide additional properties such as electronic and magnetic behaviour. This led us to a series of phosphates with stoichiometry $\text{M}^{\text{III}}\text{H}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ (where M^{III} is reported to include Al, Ga, Fe, Mn, V, Cr),⁵ where significant intercalation behaviour is suggestive of a layered structure.^{6,7} It is also worth noting that $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ already has commercial applications, including as an environmentally-friendly anticorrosion pigment in paints and coatings for metal surfaces⁸ and as an

adsorbent.⁹ Despite this, these phases have remained relatively poorly understood and exploited, mainly as a result of the limited structural data available.

In an attempt to clarify the potential of these materials we have undertaken a detailed synthetic and structural study of this family of phases. As a result, we report here a crystal structure for $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ and discuss the significance and potential of its features.

$\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ was prepared from a phosphoric acid flux reaction‡ and a single crystal was obtained for a single crystal X-ray diffraction study. Despite limitations in the size and quality of the crystal a potential structure was obtained.§ To confirm this structure was representative of the bulk sample, X-ray powder diffraction data were collected.¶ These powder data, which matched those previously reported for this material,¹⁰ were analysed using the Rietveld refinement method, with a structural model obtained from the single crystal diffraction data. Following refinement, an excellent fit was obtained between observed and calculated data and is shown in Fig. 1.† Subsequent discussion of the structure will refer to the final structural details obtained from the Rietveld analysis, although those obtained from the single crystal diffraction study were not significantly different.

The structure observed for $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ (see Fig. 2) is of two-dimensional character, containing layers of hydrogen triphosphate ($\text{H}_2\text{P}_3\text{O}_{10}^{3-}$) units, providing octahedral coordination to the Al^{3+} and stretching across the width of the layer, with the terminal hydroxyl groups protruding into the interlayer region. The layers appear to be held together by a hydrogen bonding

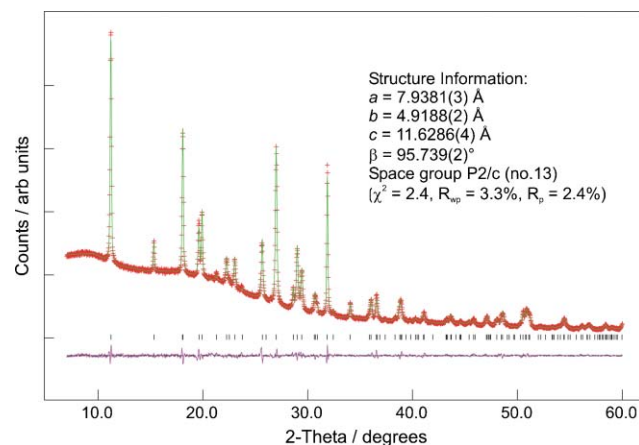


Fig. 1 Final observed (+), calculated (solid line) and difference (below) X-ray powder diffraction profile for the Rietveld refinement of $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$. Reflection positions are also marked.

^aSchool of Chemistry, University of Birmingham, Birmingham, UK B15 2TT. E-mail: a.j.wright@bham.ac.uk; Fax: +44 121 4144446; Tel: +44 121 4144406

^bInnophos Inc., 259 Prospect Plains Rd, PO Box 8000, Cranbury, NJ 08512, USA. E-mail: John.Godber@INNPHOS.com.; Fax: +1-609-860-0138; Tel: +1-609-495-2495

† Electronic supplementary information (ESI) available: Atomic coordinates and selected bond distances and angles from single crystal and powder diffraction data, FT-IR data, TGA data, ³¹P MAS NMR. See DOI: 10.1039/b514246f

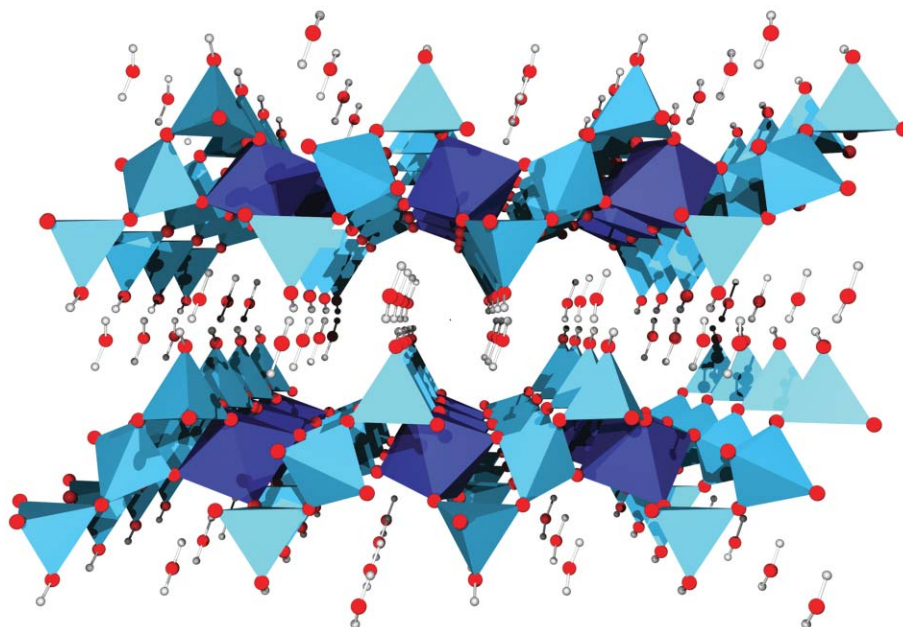


Fig. 2 Structure of $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, with AlO_6 octahedra in dark blue, PO_4 tetrahedra in light blue and hydrogen atoms as grey spheres.

network, principally involving the presence of two water molecules per formula unit within the interlamellar region, which are each hydrogen bonded to the hydroxyl groups of the hydrogen triphosphate. These metal phosphate layers have a corrugated appearance and appear to interlock into each other as the protruding hydroxyl groups align with the “groove” between hydroxyl groups in adjacent layers. These layers lie perpendicular to the a axis, with the interlayer repeat distance equal to $\sim 8 \text{ \AA}$ (*i.e. a*).

The presence in $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ of only relatively weak scattering atoms with respect to X-ray diffraction has allowed the clear determination of oxygen positions and the tentative assignment of proton positions. This has provided sensible bond lengths and angles to these species, in particular the location of water molecules within the interlayer region. We intend to use neutron powder diffraction data from deuterated samples to confirm these positions and to fully describe the hydrogen bonding network linking these layers.

The connectivity within a layer between a P_3O_{10} group and Al is shown in Fig. 3. P_3O_{10} groups are usually compared through P–P distances, P–O–P and P–P–P angles, and for $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ these values are $2.901(5) \text{ \AA}$, $132.0(7)^\circ$ and $127.0(5)^\circ$, respectively and are typical of a P_3O_{10} group, as shown by comparison with $\text{Al}(\text{NH}_4)\text{HP}_3\text{O}_{10}$ (P–P = 2.919 \AA , P–O–P = 132.2° and P–P–P = 127.7°).¹¹ In addition, individual bond lengths and angles within the P_3O_{10} group are also typical for such a group. The P–O bond lengths vary from $1.473(6) \text{ \AA}$ to $1.604(7) \text{ \AA}$, with the longest ($1.572(8) \text{ \AA}$ and $1.604(7) \text{ \AA}$) associated with the bridging oxygen (*i.e.* O(5)) in the triphosphate chain. Each AlO_6 octahedron is formed from four triphosphate groups, with two of them connected in bidentate fashion along a common edge of the octahedron.

Thermogravimetric analysis was in agreement with the stoichiometry of $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$: a mass loss between 100°C and 250°C corresponded to the loss of the interlayer water (observed 11.5%,

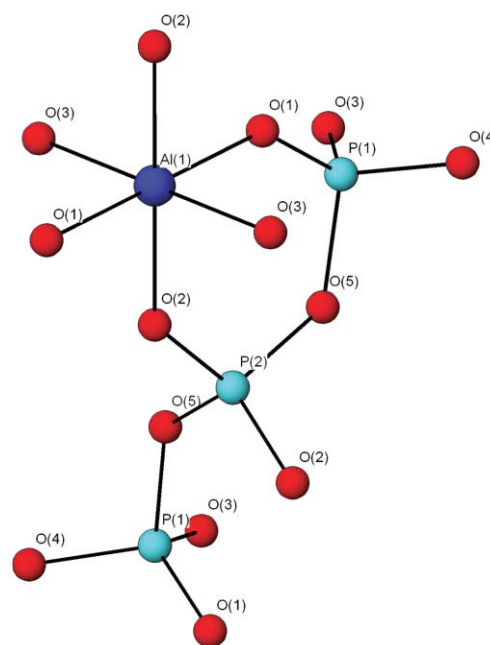


Fig. 3 Local structure of the P_3O_{10} and Al within layers in $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$.

expected 11.3%) to yield an anhydrous form, $\text{AlH}_2\text{P}_3\text{O}_{10}$, for which the structure is presently unknown. The second mass loss between 450°C and 550°C corresponded to the loss of one molecule of constitutional water (observed 5.8%, expected 6.4%) which occurs upon condensation of the triphosphate group to form the polyphosphate species, $\text{Al}(\text{PO}_3)_3$.¹²

The IR spectrum of $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ displayed bands at around 3570 and 1700 cm^{-1} which were assigned to stretching and deformation vibrations of the water molecules.† The band at around 3520 cm^{-1} was assigned to the $-\text{OH}$ vibration in the

triphosphate chain. The bands in the 1210–960 cm⁻¹ region have been associated with the P–O vibrations of the PO₄ groups in the triphosphate unit.

The P₃O₁₀ unit exhibits a binary axis of symmetry through the central phosphorus atom, which is not uncommon for such materials.¹¹ This provides two crystallographically distinct phosphorus atoms and five oxygen atoms in each triphosphate unit. A recent MAS NMR study has reported three distinct P environments in AlH₂P₃O₁₀·2H₂O, with two apparently similar but distinct environments for the terminal P sites.⁶ We have undertaken a similar NMR study on our sample and confirmed this observation.† Despite this, a thorough evaluation of our diffraction data finds no evidence of an extra terminal P site, even through a lowering of symmetry. Such discrepancies between the averaged long range structural detail available from diffraction and local detail available from NMR are not uncommon.³¹ P NMR is extremely sensitive to small site differences and here the terminal P site is within a hydrogen phosphate group which is hydrogen bonded to water, thus providing scope for localised ordering which may be undetectable with our diffraction data. We are therefore confident in the validity of our overall structure but we do not discount the possibility that a lowering of local symmetry may occur and we will seek to clarify this in our future studies.

In summary, the structure we report for AlH₂P₃O₁₀·2H₂O is one that contains many structural features common to the layered zirconium phosphates, particularly the presence of hydroxyl groups protruding into an interlamellar region occupied by water molecules. We therefore expect AlH₂P₃O₁₀·2H₂O to display many of the properties previously observed for these zirconium phosphate materials. In addition, this work provides a structure-type for the remainder of the M^{III}H₂P₃O₁₀·nH₂O (where M is a trivalent metal cation) series, supported by some preliminary studies indicating chromium, gallium and iron analogues are indeed isostructural to AlH₂P₃O₁₀·2H₂O. This work has therefore revealed a range of layered structures which suggest numerous potential properties, including conductivity, catalysis and magnetic behaviour and an ability to act as hosts in novel organic–inorganic hybrid materials.

The authors would like to thank EPSRC for a studentship for SKR and EPSRC/Innophos for a studentship for NJC. We would also like to thank Dr Simon Kitchin for his assistance in collection of the solid state NMR data.

Notes and references

‡ Experimental: AlH₂P₃O₁₀·2H₂O was prepared from a phosphoric acid flux reaction involving a mixture of H₃PO₄ (85%, Aldrich) and Al₂O₃ (99.9% Aldrich) in a molar ratio of P : Al of 6 : 1. This mixture was heated to 240 °C for 24 h and then slow cooled to room temperature over a period of 48 h, after which the white microcrystalline product was collected by filtration and washed with water.

§ Single crystal X-ray diffraction data were collected on AlH₂P₃O₁₀·2H₂O, at ambient temperature on a Bruker Smart 6000 diffractometer equipped with a copper tube source (with a graphite monochromator) and a CCD detector system. The crystal structure was solved and refined using Shelx97.¹³ **Resulting single crystal data:** H₆AlO₁₂P₃, *M* = 317.94, crystal system: monoclinic, space group *P2/c* (no.13), *a* = 7.9659(8), *b* = 4.9180(6), *c* = 11.6355(12) Å, β = 95.851(7)°, *V* = 453.46(9) Å³, *Z* = 2, *T* = 296 K, μ = 7.724 mm⁻¹, crystal size 0.22 × 0.04 × 0.02 mm, 2051 reflections measured, 742 unique (*R*_{int} = 0.07) which were used in all calculations. *R*₁ = 0.069. The final *wR2*(*F*²) was 0.147 (all data). CCDC 288341. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514246f

¶ **Powder X-ray diffraction data collection and Rietveld refinement:** The powder diffraction data (5 ≤ 2θ ≤ 100° with step size = 0.019° and step time = 7 s) were collected on a Siemens D5000 diffractometer using a primary beam Ge monochromator providing Cu-Kα₁ radiation. These data were analyzed using the Rietveld method¹⁴ through the GSAS suite of programs¹⁵ to confirm the structure and determine the bulk purity of the samples. The method used to treat the background was the linear interpolation function. The peak shape function used was Simpson's rule integration of a pseudovoigt function^{16,17}. All atom positions and isotropic displacement parameters (except the H atoms which were obtained from the single crystal model) were refined. A preferred orientation parameter was also refined in the [100] direction using the March–Dollase model.^{18,19} final ratio = 1.2032. **Resulting powder crystal data:** H₆AlO₁₂P₃; *M* = 317.94, monoclinic, *a* = 7.9381(3), *b* = 4.9188(2), *c* = 11.6286(4) Å, β = 95.739(2)°, *V* = 451.78(4) Å³, space group *P2/c* (no.13), *Z* = 2, *T* = 298 K. Final refinement gave *R*_{wp} = 3.3%, *R*_p = 2.4%, χ² = 2.4 for 419 reflections and 82 parameters.

- 1 *Handbook of Layered Materials*, ed. S. C. Auerbach, K. A. Carrado and P. K. Dutta, Marcel Dekker Ltd., New York, 2004.
- 2 D. Schmidt, D. Shah and E. P. Giannelis, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 205.
- 3 E. R. Kleinfeld and G. S. Ferguson, *Science*, 1994, **265**, 370.
- 4 G. Alberti, M. Casciola, U. Costantino and R. Vivani, *Adv. Mater.*, 1996, **8**, 291.
- 5 F. D'Yvoire, *Bull. Soc. Chim. Fr.*, 1962, **6**, 1224–1236; P. P. Mel'nikov, V. A. Efremov, A. K. Stepanov, T. S. Romanova and L. N. Komissarova, *Russ. J. Inorg. Chem.*, 1976, **21**, 26–28; M. A. G. Aranda, J. Chaboy and S. Bruque, *Inorg. Chem.*, 1991, **30**, 2394–2397; V. A. Lyutsko and A. F. Selevich, *Zh. Neorg. Khim.*, 1983, **28**, 923–926; P. Remy and A. Boule, *Bull. Soc. Chim. Fr.*, 1972, **6**, 2213.
- 6 A. Hayashi, H. Nakayama, T. Eguchi, N. Nakamura and M. Tsuchioka, *J. Inclusion Phenom. Macroscopic Chem.*, 1999, **34**, 401–412.
- 7 V. A. Lyutsko, A. V. Tuchkovskaya and A. L. Shifrina, *Russ. J. Inorg. Chem.*, 1987, **32**, 11, 1541–1544.
- 8 Y. Taketani and H. Kondo, *Eur. Pat. 0845508*, 1998.
- 9 M. Okuda and M. Kobayashi, *JP Pat. 4109954*, 1992.
- 10 A. W. Frazier and K. R. Waerstad, *Ind. Eng. Chem. Res.*, 1993, **32**, 8, 1760–1766.
- 11 M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel, *Acta Crystallogr., Sect. B*, 1977, **B33**, 1436–1438.
- 12 L. Pauling and J. Sherman, *Z. Kristallogr.*, 1937, **96**, 481–487.
- 13 G. M. Sheldrick, *SHELX97 - Programs for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- 14 H. M. Rietveld, *Acta Crystallogr.*, 1967, **22**, 151.
- 15 A. C. Larson and R. B. Von Dreele, *General Structure Analysis System*, Los Alamos National Laboratory, 1994.
- 16 C. J. Howard, *J. Appl. Crystallogr.*, 1982, **15**, 615–620.
- 17 P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79–83.
- 18 A. March, *Z. Kristallogr.*, 1932, **81**, 285–297.
- 19 W. A. Dollase, *J. Appl. Crystallogr.*, 1986, **19**, 267–272.