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Synthesis and characterization of $NH_4(Al_{0.64}Ga_{0.36})(HPO_4)_2$; a three dimensional anionic tunnel structure with charge balancing NH_4^+

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$NH_4(Al_{0.64}Ga_{0.36})(HPO_4)_2$ was prepared hydrothermally and examined by single crystal X-ray diffraction. It consists of corner-sharing MO_6 octahedra and PO_4 tetrahedra and is structurally related to $NH_4Fe(HPO_4)_2$ but distinct from $H_3O\cdot Fe(HPO_4)_2$. The ammonium ions lie in a 3D connected network of tunnels with dimensions smaller than those found in zeolite A: $a=7.109(4)$, $b=8.695(4)$, $c=9.252(6)$ Å, $\alpha=65.01(4)$, $\beta=70.25(5)$, $\gamma=69.01(4)°$, $V=472.1(4)$ Å^3, space group $P\bar{1}$, $Z=3$, $D_m=2.63$ g cm^{-3}, $D_c=2.66$ g cm^{-3}, 168 parameters, 1916 reflections, $R_F=0.056$ (all data).

Aluminium and gallium phosphates have received considerable attention since Wilson *et al.*[1] reported the preparation of zeolitic aluminophosphates (AlPOs) in 1982. However, there had been a number of reports, prior to this, describing AlPOs that were possible byproducts during the production and use of phosphoric acid,[2] mineral related phases, or possible products from the reaction of phosphate containing fertilizers with soil minerals.[3,4] Typically, the materials produced during these studies were incompletely characterized.

The preparation of microporous AlPO materials is often performed in the presence of structure directing or templating agents; these additives are usually organoamines or organoammonium salts. Recently, there have been several reports addressing the use of chiral coordination complexes as possible templates for chiral AlPO and gallophosphate frameworks.[5–9] The present paper reports the synthesis and structure of $NH_4(Al_{0.64}Ga_{0.36})(HPO_4)_2$. This material was prepared accidentally while exploring the use of different aluminium and gallium sources for the synthesis of the chiral 3D phase Λ-$Co(en)_3[H_3Ga_{2-x}Al_xP_4O_{16}]$[10] (en = 1,2-diaminoethane).

Experimental

Gallium- and aluminium-containing gels were prepared from gallium trichloride (Strem) and aluminium trichloride hexahydrate (certified granules, Fisher). 0.04 mol of each of the salts was dissolved in separate 150 ml portions of water, and the solutions were cooled with ice. Gels were formed by the slow addition of concentrated ammonium hydroxide to each of the solutions. After filtering and drying, they were heated at 125 °C under dynamic vacuum to remove as much ammonium chloride as possible by sublimation. Powder diffraction data revealed that small amounts of residual ammonium chloride were present in the dry gels. The metal content of the products was estimated thermogravimetrically. The amorphous gels were then mechanically combined to give a material with a 1 : 1 Ga : Al ratio.

Colorless crystals of $NH_4(Al_{1-x}Ga_x)(HPO_4)_2$ were obtained from a reaction mixture with starting composition $Co(en)_3^{3+}$: Al : Ga : P : TMAOH : H_2O of 0.25 : 1 : 1 : 2.86 : 2 : 90 (TMAOH = tetramethylammonium hydroxide). Λ-$Co(en)_3^{3+}$ was present in the mixture, as we were exploring its use as a template. The aluminium/gallium source was suspended in half of the necessary water. The orthophosphoric acid (Fisher) was mixed with the remaining water and added to the slurry while stirring. The resulting white gel was stirred for 3.5 h at room temperature and then the TMAOH was added. The metal complex $[\Lambda$-$Co(en)_3(H_2PO_4)_3]$ was then added, and the orange mixture was stirred for 1 h and placed in 23 ml Teflon-lined acid digestion bombs for 4 days at 130 °C.

The product from the hydrothermal synthesis consisted of *ca.* 5–10% colorless prisms, along with a colorless microcrystalline material. The absence of color indicated that none of the metal complex was incorporated into the solid products. The density of several representative colorless prisms was measured by the flotation method using carbon tetrachloride and 1,1,2,2-tetrabromoethane. A powder X-ray diffraction pattern of the bulk product was measured using a Scintag X1 diffractometer equipped with a Peltier cooled solid state detector. A small amount of material consisting of 80–90% colorless prisms (estimated by inspection under an optical microscope) was separated from the rest of the product by flotation in a mixture of 1,1,2,2-tetrabromoethane and 1,2-dibromoethane. This sample was analyzed for nitrogen content by Atlantic Microlabs, Inc. of Norcross, Georgia, USA.

Single crystal diffraction data were collected using an Enraf-Nonius CAD4 diffractometer. The unit cell parameters were determined using 25 reflections in the range 22–73° 2θ. Data was collected using θ–2θ scans and reduced using components of the NRCVAX package.[11] The structure was solved by direct methods using SHELXS-86,[12] completed using difference Fourier syntheses, and refined using SHELXL-93.[13] The Al : Ga for each of the metal sites was refined subject to the constraint that both sites were fully occupied. Initially, a ψ-scan based semiempirical absorption correction was employed. However, this led to physically unrealistic anisotropic temperature factors in the final stages of the refinement. Subsequently, the data reduction was performed without merging any reflections, the structure was refined using isotropic temperature factors, and an empirical absorption correction was applied using the program XABS2[14] (relative min./max. transmission factors 0.674/1.192) prior to the refinement of anisotropic temperature factors for all of the atoms. This approach led to physically realistic thermal ellipsoids. No hydrogen atom positions could be located crystallographically. Details of the data collection and structure refinement can be found in Table 1, refined positions and occupancies are given in Table 2, some selected distances and angles are given in Table 3, and the labelling is illustrated in Fig. 1. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/70.

Table 1 Crystal data and structure refinement for $(NH_4)(Al_{0.64}Ga_{0.36})(HPO_4)_2$

formula	$(NH_4)(Al_{0.64}Ga_{0.36})(HPO_4)_2$
formula weight	252.32[a]
temperature, wavelength	ambient, 1.54056 Å
crystal system, space group	triclinic, $P\bar{1}$
unit cell dimensions	$a=7.109(4)$ Å, $\alpha=65.01(4)°$ $b=8.695(4)$ Å, $\beta=70.25(5)°$ $c=9.252(6)$ Å, $\gamma=69.01(4)°$
Z, volume	3, 472.1(4) Å^3
$D_c(D_m)$	2.66(2.63) g cm^{-3}
absorption coefficient	9.14 mm^{-1}
absorption correction	empirical (XABS2)
$F(000)$	361
crystal size	$0.05 \times 0.1 \times 0.1$ mm
θ range for data collection	5.40–74.74°
index ranges	$-8<h<8$, $-10<k<10$, $-1<l<11$
reflections collected	2261
independent reflections	1916 ($R_{int}=0.0846$)[b]
data/restraints/parameters	1916/0/168
goodness-of-fit on F^2	1.127
final R indices $[I>2\sigma(I)]$[b]	$R_1=0.0524$, $wR_2=0.1496$
R indices (all data)[b]	$R_1=0.0560$, $wR_2=0.1522$
largest diff. peak, hole	1.388, -0.770 e Å^{-3}

[a] Includes hydrogen that was not located crystallographically.

[b] $R_{int}=\sum|F_o^2-F_o^2(\mathrm{mean})|/\sum[F_o^2]$, $R=\sum||F_o|-|F_c||/\sum|F_o|$, $R_F^2=\{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $(NH_4)(Al_{0.64}Ga_{0.36})(HPO_4)_2$; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U_{eq}
Al(1)[a]	5000	0	5000	6(1)
Ga(1)[b]	5000	0	5000	6(1)
Al(2)[c]	7031(1)	2170(1)	−527(1)	6(1)
Ga(2)[d]	7031(1)	2170(1)	−527(1)	6(1)
P(1)	4194(2)	3769(2)	2298(1)	8(1)
P(2)	5870(2)	−1505(1)	2178(1)	7(1)
P(3)	10 533(2)	−538(1)	−2205(1)	7(1)
O(1)	3496(5)	2373(4)	3881(4)	11(1)
O(2)	4779(5)	3168(4)	854(4)	11(1)
O(3)	7490(5)	4481(4)	−2039(4)	10(1)
O(4)	6119(6)	4147(5)	2492(4)	15(1)
O(5)	6678(5)	−124(4)	679(4)	10(1)
O(6)	5213(5)	2514(4)	−1853(4)	11(1)
O(7)	4453(5)	−830(4)	3561(4)	11(1)
O(8)	7820(5)	−2985(4)	2790(4)	14(1)
O(9)	9306(5)	1273(4)	−2084(4)	9(1)
O(10)	2395(5)	−326(4)	6396(4)	13(1)
O(11)	11 062(5)	−1891(4)	−612(4)	10(1)
O(12)	9136(6)	−1307(5)	−2598(5)	17(1)
N(1)	11 215(9)	−3381(7)	−4723(6)	27(1)
N(2)	10 000	−5000	0	28(2)

[a] Occupancy = 0.565(8). [b] Occupancy = 0.435(8). [c] Occupancy = 0.680(6). [d] Occupancy = 0.320(6).

Table 3 Selected bond lengths (Å) for $(NH_4)(Al_{0.64}Ga_{0.36})(HPO_4)_2$

2 × Al(1)—O(10)	1.905(4)	P(1)—O(3)	1.545(3)
2 × Al(1)—O(7)	1.951(3)	P(1)—O(4)	1.598(4)
2 × Al(1)—O(1)	1.959(3)	P(2)—O(5)	1.498(4)
Al(2)—O(2)	1.873(4)	P(2)—O(6)	1.521(3)
Al(2)—O(11)	1.877(4)	P(2)—O(7)	1.529(4)
Al(2)—O(5)	1.890(4)	P(2)—O(8)	1.593(4)
Al(2)—O(6)	1.937(4)	P(3)—O(10)	1.509(4)
Al(2)—O(9)	1.942(4)	P(3)—O(11)	1.513(3)
Al(2)—O(3)	1.972(4)	P(3)—O(9)	1.533(3)
P(1)—O(2)	1.513(4)	P(3)—O(12)	1.578(4)
P(1)—O(1)	1.518(4)		

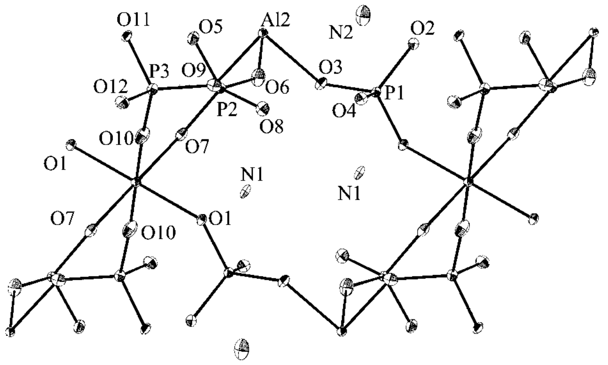

Fig. 1 ORTEP diagram showing the naming scheme used to describe the structure. The view is along the *a*-axis. The shortest oxygen–oxygen contact across the tunnel [O(8) to O(8)] is greater than 5 Å.

Results and Discussion

Powder X-ray diffraction indicated that the bulk product from the hydrothermal synthesis consisted of 5–10% $NH_4(Al_{0.64}Ga_{0.36})(HPO_4)_2$ (single crystals) along with a large amount of a leucophosphite type phase (polycrystalline material).[15,16] The single crystal X-ray diffraction study demonstrates that the colorless prisms have a framework consisting of corner sharing MO_6 octahedra and PO_4 tetrahedra. The P—O bond lengths clearly indicate that one oxygen in each of the three crystallographically distinct PO_4 groups is protonated, while the other three oxygens are bridging. There are two distinct MO_6 octahedra, both of which contain a mixture of gallium and aluminium that is significantly different from that in the starting synthesis gel. While both octahedral metal sites show a preference for aluminium over gallium, the occupancies and mean M—O bond lengths (⟨M(1)—O⟩ = 1.938 Å, ⟨M(2)—O⟩ = 1.915 Å) indicate that the M(2) site has a slightly stronger preference for aluminium than the M(1) site.

The framework is relatively dense, with a three-dimensional network of small tunnels housing charge balancing species (see Fig. 2). The structure indicates an overall composition of $X[(Al_{0.64}Ga_{0.36})(HPO_4)_2]$, where X is the charge balancing species. The measured crystal density, known composition of the synthesis gel, and X-ray data, are consistent with X being either NH_4^+ or H_3O^+. However, the nitrogen analysis for a sample consisting of 80–90% colorless prisms indicated the presence of *ca.* 4.5% nitrogen (5.5% expected if $X=NH_4^+$ and the sample was pure) supporting the assignment of X as NH_4^+. For the compound $NH_4[(Al_{0.64}Ga_{0.36})(HPO_4)_2]$ the expected density is 2.66 g cm^{-3} while the observed density was 2.63 g cm^{-3}. An examination of the literature indicates that the material under study is isostructural with $NH_4Fe(HPO_4)_2$,[17] but structurally distinct from $H_3OFe(HPO_4)_2$.[18] This observation, combined with the relatively high final pH of the synthesis gel (*ca.* 5.5) that was employed, and the nitrogen analysis indicate that the species in the tunnel system are NH_4^+. While no hydrogen positions could be located crystallographically, an examination of the coordination environment around the two distinct nitrogen sites showed that there were many relatively short N—O distances [for N(1) three contacts <3 Å and ten <3.5 Å, and for N(2) two <3 Å and twelve <3.5 Å] indicating that there is hydrogen bonding between framework oxygens and the ammonium ions.

The tunnels running through the structure are smaller than those found in a zeolite such as LTA (free diameter of *ca.* 4.1 Å, minimum O···O distance *ca.* 6.8 Å), but comparable in size to those found in ion exchangeable materials such as the NASICONs.[19,20] When viewed in projection, the channels running parallel to the crystallographic *a*-axis are >4 Å in diameter (the shortest oxygen–oxygen distance across the pore is >5 Å), those running parallel to the crystallographic *b*-axis have an approximate diameter of 3.5 Å, and those running parallel to the crystallographic *c*-axis are elliptical with approximate dimensions 3.5×8 Å (all dimensions are O···O distances).

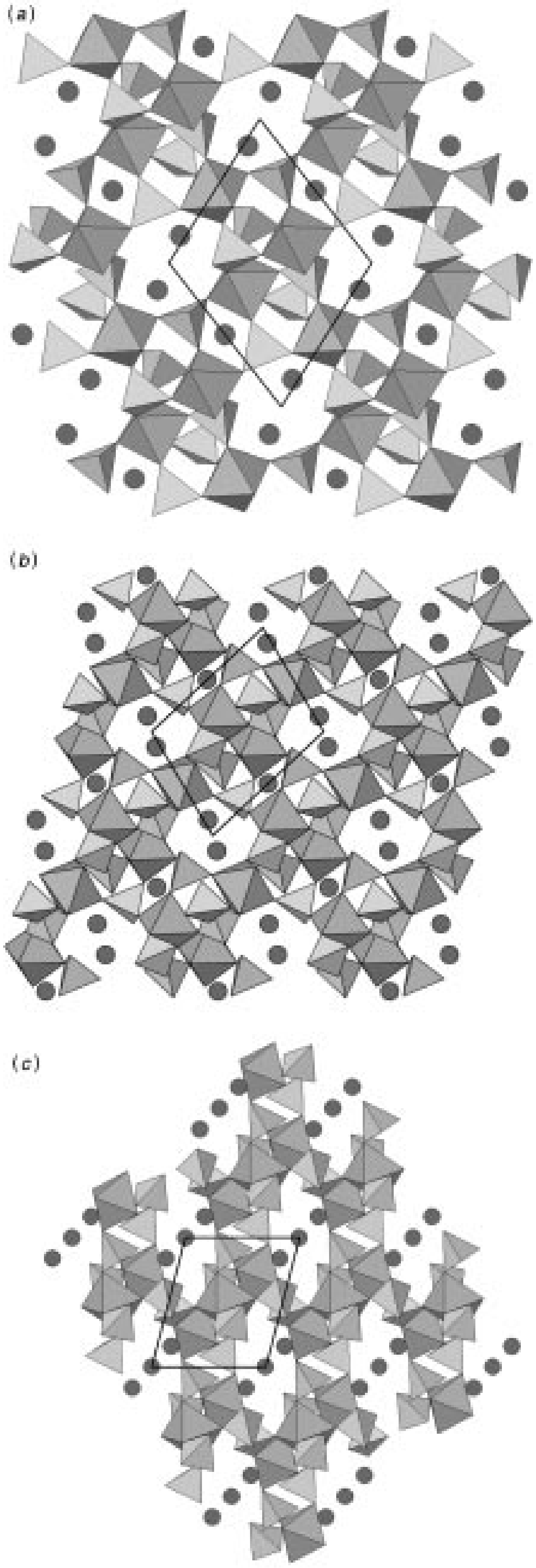

Fig. 2 Projections of the structure along the (*a*) *a*-axis, (*b*) *b*-axis and (*c*) *c*-axis showing the connectivity of the framework and the locations of the NH_4^+ in the channel system

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References

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
2 L. M. Lapina, I. A. Grishina, N. I. Usacheva and N. L. Portnova, *J. Appl. Chem. USSR*, 1972, **45**, 4.
3 J. F. Haseman, J. R. Lehr and J. P. Smith, *Soil Sci. Soc. Am. Proc.*, 1950, **15**, 76.
4 J. P. Smith and W. E. Brown, *Am. Miner.*, 1959, **44**, 138.
5 D. A. Bruce, *Synthesis and Characterization of Heterogeneous Metal Oxide Catalysts on Amorphous and Molecular Sieve Supports*, PhD Thesis, Georgia Institute of Technology, Atlanta, GA, 1994.
6 K. Morgan, G. Gainsford and N. Milestone, *J. Chem. Soc., Chem. Commun.*, 1995, 425.
7 D. A. Bruce, A. P. Wilkinson, M. G. White and J. A. Bertrand, *J. Chem. Soc., Chem. Commun.*, 1995, 2059.
8 D. A. Bruce, A. P. Wilkinson, M. G. White and J. A. Bertrand, *J. Solid State Chem.*, 1996, **125**, 228.
9 M. J. Gray, J. Jasper, A. P. Wilkinson and J. C. Hanson, *Chem. Mater.*, 1997, **9**, 976.
10 S. M. Stalder and A. P. Wilkinson, *Chem. Mater.*, 1997, **9**, 2168.
11 E. J. Gabe, Y. Le Page, J.-P. Charland and F. L. Lee, *J. Appl. Crystallogr.*, 1989, **22**, 384.
12 G. M. Sheldrick, *Program for the Solution of Crystal Structures*, University of Göttingen, 1986.
13 G. M. Sheldrick, *Program for Crystal Structure Determination*, Univ. of Göttingen, 1993.
14 S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53.
15 J. B. Parise, *Acta Crystallogr., Sect. C*, 1984, **40**, 1641.
16 R. C. L. Mooney-Slater, *Acta Crystallogr.*, 1966, **20**, 526.
17 O. V. Yakubovich, *Kristallografiya*, 1993, **38**, 43.
18 I. Vencato, E. Mattievich, L. d. F. Moreira and Y. P. Mascarenhas, *Acta Crystallogr., Sect. C*, 1989, **45**, 367.
19 H. Kohler and H. Schulz, *Mater. Res. Bull.*, 1985, **20**, 1461.
20 P. R. Rudolf and A. Clearfield, *J. Solid State Chem.*, 1988, **72**, 100.

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