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Poly[(2,2′-bipyridine-κ^2N,N')-(μ_2-dihydrogen phosphato-$\kappa^2O{:}O'$)-(μ_2-hydrogen phosphato-$\kappa^2O{:}O'$)-aluminium(III)], Al(2,2′-bipy)-(HPO_4)(H_2PO_4), a layered inorganic–organic hybrid material

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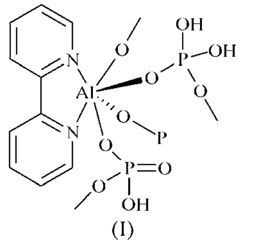
The title compound, $[Al(HPO_4)(H_2PO_4)(C_{10}H_8N_2)]_n$, consists of AlO_4N_2 octahedra vertex-linked to H_2PO_4 and HPO_4 tetrahedra to form layers based on a (4,12)-net. The layers stack in an *AAA* fashion, held in place by π–π interactions between 2,2′-bipyridine molecules coordinated to Al atoms in adjacent layers.

Comment

The use of organic amines as structure-directing agents or templates in the solvothermal synthesis of open-framework metal phosphates is well documented (Cheetham *et al.*, 1999). In a few metal phosphates, amines also act as ligands and bond *via* nitrogen to the metal centres to form MO_xN_y units within the framework. For example, in $[TH_2]_2[TH]_2[Zn_{12}(PO_4)_{10}(H_2O)_2]\cdot H_2O$ (T = 1,3-diaminopropane; Vaidhyanathan *et al.*, 1999), the diamine is present in two distinct forms, both as a free dication and as a monocation with the $-NH_2$ group bonded to zinc generating ZnO_3N as well as ZnO_4 tetrahedra within the zinc–phosphate framework. Several such metal phosphates containing MO_xN_y units have been prepared using 2,2′-bipyridine. The majority of these have chain structures in which metal and phosphorus centres are linked through oxygen bridges. Examples include phosphates of Mn (Sarneski *et al.*, 1993), Cd (Lin *et al.*, 2003) and mixed Zn–V (Finn & Zubieta, 2002). In addition, layered phosphates of Ga (Lin *et al.*, 2004), V (Lu *et al.*, 2002) and mixed Cu–V (Finn & Zubieta, 2000) are also known, in which the metals coordinate to 2,2′-bipyridine. In this work, the first aluminium phosphate (AlPO) incorporating 2,2′-bipyridine is described. The structure of the title compound, (I), differs from that of all previously reported AlPOs in that it has direct Al—N bonding, giving rise to unusual AlO_4N_2 units with octahedral coordination.



(I)

The Al atom, like all the atoms in the asymmetric unit, lies on a general position with average Al1—N and Al1—O distances of 2.075 (16) and 1.86 (3) Å, respectively (Table 1). These average bonding distances are similar to those found in other octahedrally coordinated aluminium compounds in which aluminium is coordinated to 2,2′-bipyridine (Bellavance *et al.*, 1977) or constitutes part of an AlPO framework (Kniep *et al.*, 1978), respectively. Atom Al1 is connected *via* Al—O—P bridges to two crystallographically distinct P atoms, *viz.* P1 and P2, both of which have two terminal P—O bonds to complete the tetrahedral coordination. The O—P—O angles lie in the range 106.6 (1)–114.1 (1)°. Linkages P1—O2, P1—O3 and P2—O7 constitute POH groups, as confirmed both by the location of H atoms in the difference Fourier maps and by bond-valence calculations (Brese & O'Keeffe, 1991) (Fig. 1). The remaining terminal linkage, P2—O6, has some degree of multiple-bond character, although hydrogen-bonding interactions between atom O6 and neighbouring POH groups (see below) leads to a lengthening of this bond compared with a free P═O bond. The $Al1O_4N_2$, H_2P1O_4 and $HP2O_4$ units link through their vertices to generate infinite undulating neutral layers of formula $[Al(HPO_4)(H_2PO_4)(C_{10}H_8N_2)]$, which lie in the *bc* plane and stack in an *AAA* sequence along the *a* axis. The layers can be described as consisting of four-membered rings of alternating $Al1O_4N_2$ and H_2P1O_4 units linked

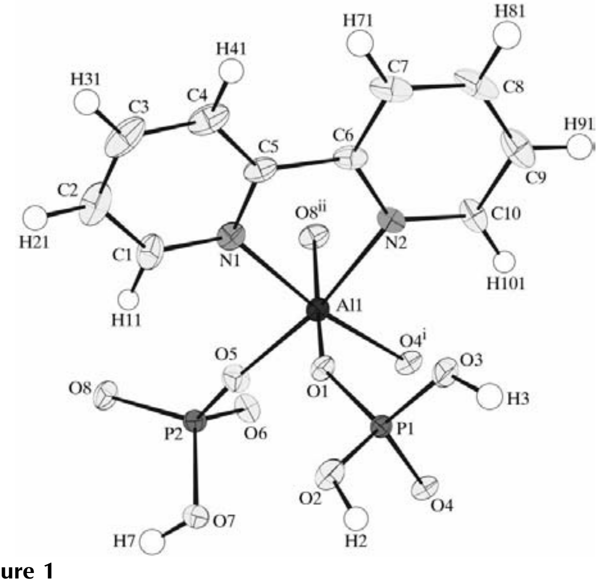


Figure 1
The local coordination of atoms in $[Al(HPO_4)(H_2PO_4)(C_{10}H_8N_2)]$ (50% probability displacement ellipsoids). [Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.]

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together by bridging HP2O$_4$ units to give 12-membered rings with cross-pore oxygen-to-oxygen distances O1$^{\rm i}\cdots$O1$^{\rm ii}$ = 8.510 (3) Å, O2$^{\rm i}\cdots$O2$^{\rm ii}$ = 7.679 (4) Å and O7$^{\rm i}\cdots$O7$^{\rm ii}$ = 5.172 (3) Å (Fig. 2). Within the 12-membered rings, there are strong hydrogen bonds involving the terminal P2—O6 groups and P1—OH and P2—OH groups (Table 2). The bidentate bipyridine groups bonded to atom Al1 lie perpendicular to the AlPO (4,12)-net (Wells, 1984) and project into the interlayer space (Fig. 3). The shortest distance between 2,2′-bipyridine molecules on adjacent layers is 3.386 (4) Å, suggesting some degree of π–π interaction.

[Al(HPO$_4$)(H$_2$PO$_4$)(C$_{10}$H$_8$N$_2$)] is isostructural with a reported layered gallium phosphate (Lin *et al.*, 2004). The structure is also closely related to that of [Mn(HPO$_4$)(H$_2$PO$_4$)(C$_{10}$H$_8$N$_2$)] (Sarneski *et al.*, 1993). In the latter, the four-membered rings of Mn$_2$P$_2$ units link through further phosphate groups to give a linear polymeric array rather than the layered structure observed here.

The title structure does, however, possess several features that are rare in AlPOs. Firstly, the layers are not charged; all other layered AlPOs have negatively charged metal–phosphate layers with positively charged species, *e.g.* alkali-metal or amine cations, between the layers. Secondly, the mixed oxygen–nitrogen octahedral coordination of aluminium is unknown in AlPOs, although AlO$_4$N$_2$ units have been observed previously in an aluminophosphinate dimer and related polymer (Wang *et al.*, 2000). In a typical contrasting example, an AlPO prepared in the presence of 4,4′-bipyridine, *viz.* (C$_{10}$H$_9$N$_2$)[Al(PO$_4$)(H$_2$PO$_4$)], which has the same Al:P ratio of 1:2 as the title compound, has an AlPO framework consisting of negatively charged chains of linked AlO$_4$ and PO$_4$ tetrahedra held together by hydrogen bonding between the framework O atoms and the 4,4′-bipyridine cations (Chippindale & Turner, 1997).

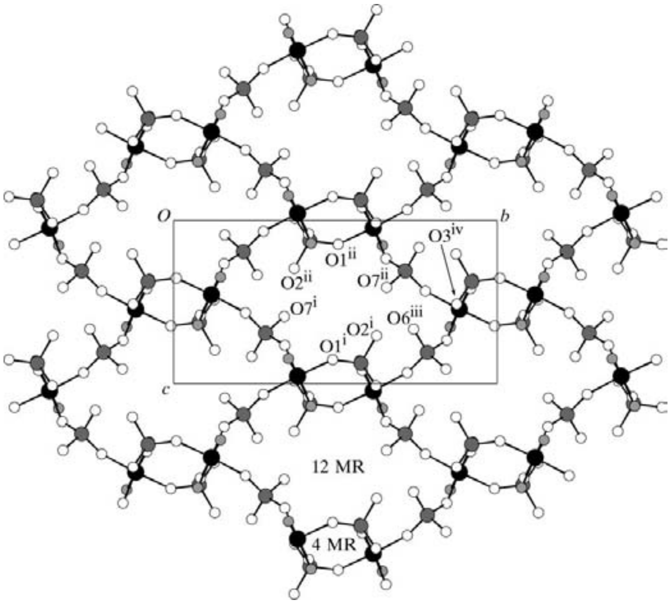

Figure 2
A view along the *a* axis of one layer of the title compound, showing the (4,12)-network formed from linking octahedral AlO$_4$N$_2$ and tetrahedral HPO$_4$ and H$_2$PO$_4$ units. The four- and 12-membered rings (4 and 12 MR) referred to in the *Comment* are labelled, together with atoms O1, O2 and O7. The C atoms of 2,2′-bipyridine and all H atoms have been omitted. Short O$\cdots$O contacts, indicative of intralayer hydrogen bonds, occur between the terminal O6 group and the O2—H, O3—H and O7—H groups. Key: Al black spheres, P grey spheres, O white spheres and N small grey spheres. [Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y+1, z$.]

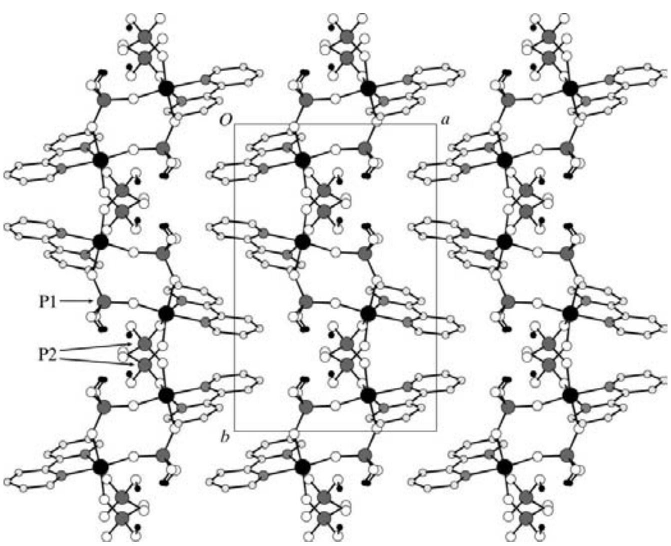

Figure 3
A view along the *c* axis showing the stacking of the layers. Key as for Fig. 2, with small black spheres representing H atoms.

Experimental

Single crystals of [Al(HPO$_4$)(H$_2$PO$_4$)(C$_{10}$H$_8$N$_2$)] were prepared under solvothermal conditions. Aluminium isopropoxide (1 g) was dispersed in butan-2-ol (7.86 ml) by stirring, followed by addition of 2,2′-bipyridine (1.835 g) and a small amount of Si(OEt)$_4$ (0.1 ml), which acts as a mineralizer. Aqueous H$_3$PO$_4$ (0.63 ml, 85 wt%) was then added, and the gel was stirred until homogeneous, sealed in a Teflon-lined autoclave and heated at 453 K for 10 d. The solid product was collected by filtration, washed copiously with water and dried in air at 353 K. A clear colourless hexagonal plate was isolated from the bulk sample for analysis. The experimental and simulated powder X-ray diffraction patterns are in good agreement, suggesting that the sample is monophasic. Thermogravimetric analysis showed a smooth weight loss of 46.7% over the range 553–693 K, to give a black X-ray amorphous product. The observed weight loss is in good agreement with the loss of one mole of 2,2′-bipyridine (41.5%) and one mole of water (4.8%).

Crystal data

[Al(HPO$_4$)(H$_2$PO$_4$)(C$_{10}$H$_8$N$_2$)]
M_r = 376.14
Monoclinic, $P2_1/c$
a = 10.9253 (2) Å
b = 15.6992 (3) Å
c = 8.3683 (2) Å
β = 109.0658 (11)°
V = 1356.58 (5) Å^3
Z = 4
D_x = 1.842 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.43 mm^{-1}
T = 150 (2) K
Hexagonal plate, colourless
0.08 × 0.08 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.97$, $T_{\max} = 1.00$
5615 measured reflections
3079 independent reflections
2238 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\max} = 27.5°$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.041$
$S = 1.12$
2238 reflections
220 parameters
H atoms treated by a mixture of independent and constrained refinement
Modified Chebychev polynomial (Watkin, 1994) with the coefficients 0.747, 0.542 and 0.526
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Al1—O1	1.8899 (17)	P1—O2	1.5565 (17)
Al1—O4$^{\rm i}$	1.8319 (17)	P1—O3	1.5604 (18)
Al1—O5	1.8307 (17)	P1—O4	1.5075 (16)
Al1—O8$^{\rm ii}$	1.8744 (17)	P2—O5	1.5128 (16)
Al1—N1	2.063 (2)	P2—O6	1.5375 (17)
Al1—N2	2.086 (2)	P2—O7	1.5801 (17)
P1—O1	1.5013 (16)	P2—O8	1.5134 (16)
O1—Al1—O4$^{\rm i}$	92.40 (7)	O1—Al1—N2	87.15 (8)
O1—Al1—O5	90.10 (8)	O4$^{\rm i}$—Al1—N2	91.51 (8)
O4$^{\rm i}$—Al1—O5	100.33 (8)	O5—Al1—N2	167.95 (8)
O1—Al1—O8$^{\rm ii}$	170.90 (8)	O8$^{\rm ii}$—Al1—N2	85.04 (8)
O4$^{\rm i}$—Al1—O8$^{\rm ii}$	92.46 (8)	N1—Al1—N2	77.97 (8)
O5—Al1—O8$^{\rm ii}$	96.59 (8)	Al1—O1—P1	137.6 (1)
O1—Al1—N1	86.11 (8)	Al1$^{\rm i}$—O4—P1	154.29 (11)
O4$^{\rm i}$—Al1—N1	169.43 (8)	Al1—O5—P2	147.74 (12)
O5—Al1—N1	90.15 (8)	Al1$^{\rm iii}$—O8—P2	148.21 (11)
O8$^{\rm ii}$—Al1—N1	87.70 (8)		

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O6$^{\rm iv}$	0.86 (4)	1.73 (4)	2.581 (2)	169 (4)
O3—H3$\cdots$O6$^{\rm i}$	0.84 (4)	1.80 (4)	2.644 (3)	178 (4)
O7—H7$\cdots$O6$^{\rm iii}$	0.90 (4)	1.76 (4)	2.658 (3)	176 (4)

Symmetry codes: (i) $-x+1, -y, -z+1$; (iii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

H atoms attached to the 2,2′-bipyridine and phosphate units were located in difference Fourier maps. The fractional coordinates and isotropic displacement parameters of the phosphate H atoms were refined. The bipyridine H atoms were, however, positioned geometrically during the final refinement cycles and constrained to ride on their parent C atoms [C—H = 1.00 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)].

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3011). Services for accessing these data are described at the back of the journal.

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