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Assembly of Helical Hydrogen Bonds in a New Layered Aluminophosphate $[C_6N_3H_{17}][Al_2(HPO_4)(PO_4)_2]$

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A new layered aluminophosphate, $[C_6N_3H_{17}][Al_2(HPO_4)(PO_4)_2]$ (denoted AlPO–CJ21), has been prepared in an alcoholic system by the use of *N*-(2-aminoethyl)-piperazine (AEPP) as the template. Its inorganic layer containing a series of bridged six-membered rings (MRs) is a new type of 4.6-net sheet built up from AlO_4, $PO_2(OH)(=O)$, and $PO_3(=O)$ tetrahedra. Interestingly, inorganic helical chains of right- or left-handedness are presented in the aluminophosphate layers, and fascinating hydrogen-bonded helices are self-assembled under solvothermal conditions between organic templates and inorganic sheets via strong hydrogen bondings of O···N atoms. Crystal data: monoclinic, $P2_1$ (No. 4), $a = 10.069(2)$ Å, $b = 8.0875(16)$ Å, $c = 10.598(2)$ Å, $\beta = 94.71(3)°$, $z = 2$, $R_1 = 0.0325$ [$I > 2\Sigma(I)$], and w$R_2 = 0.0807$ (all data); Flack parameter: 0.03.

Introduction

The synthesis of new aluminophosphate compounds with novel porous network or framework structures has attracted considerable attention because of the potential applications of these compounds in catalysis, separation, and adsorption.[1−3] In recent years, a large variety of anionic aluminophosphates with zero-dimensional (0D) clusters, one-dimensional (1D) chains, two-dimensional (2D) layers, and three-dimensional (3D) interrupted open-framework structures have been successfully synthesized by the employment of organic amines as the templates.[4] So far, seven unique structures exist in the layered aluminophosphates with $Al_2P_3O_{12}^{3-}$ stoichiometry, including $[C_2H_8N]_2[Al_2(HPO_4)(PO_4)_2]$,[5] $[2\text{-}BuNH_3]_2[HAl_2P_3O_{12}]$,[6] $[pyH][H_2Al_2P_3O_{12}]$ (py = pyridine),[6] $[C_5H_9NH_3]_2[Al_2P_3O_{12}H]$,[7] $[C_6H_{11}NH_3]_2[Al_2P_3O_{12}H]$,[8] $[C_6NH_8][Al_2P_3O_{10}(OH)_2]$,[9] and $[C_9H_{20}N][Al_2(HPO_4)_2(PO_4)]$.[10]

It is well-known that multiple hydrogen-bonded networks are usually formed in host−guest assembly systems and dramatically influence the formation of 2D layered materials.[11−15] Our recent studies also found that hydrogen bonds play a significant role in determining stereospecificity between the host frameworks and the templates in open-framework metal phosphates.[16] Helical hydrogen bonds formed by the guest molecules and the inorganic hosts are particularly rare in organically templated microporous aluminophosphates and related materials. To our knowledge, only two examples have such character. One is the extra-large-pored aluminophosphate VPI-5 with triple helices of water molecules inside the 18-membered-ring (MR) chan-

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nels,[17] and the other is the layered aluminophosphate $[C_2H_8N]_2[Al_2(HPO_4)(PO_4)_2]$ with double hydrogen-bonded helical chains formed by the organic templates and the inorganic network.[5] In this paper we report a new layered $Al_2P_3O_{12}^{3-}$ aluminophosphate, $[C_6N_3H_{17}][Al_2(HPO_4)(PO_4)_2]$ (AlPO−CJ21), with inorganic helical chains and hydrogen-bonded helices assembled under solvothermal conditions.

Experimental Section

Synthesis and Characterization. AlPO−CJ21 was prepared from the alcoholic system $1.0Al(^iPrO)_3/4.5H_3PO_4/1.5AEPP/15.3TEG$ (AEPP = *N*-(2-aminoethyl)-piperazine; TEG = triethylene glycol) at 180 °C for 9 days. First, $Al(^iPrO)_3$ (0.20 g, 0.98 mmol) was dispersed into TEG (2.24 g, 14.94 mmol) followed by the addition of AEPP (0.20 g, 1.52 mmol). Then H_3PO_4 (0.51 g, 4.42 mmol; 85 wt %) was slowly added to the above mixture. The gel was sealed in a Teflon-lined stainless steel 15-mL autoclave and heated at 180 °C for 9 days. The final product consisting of large platelike single crystals was washed with distilled water and dried in the air at room temperature.

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300Dv spectrometer. Elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. After AlPO−CJ21 was pretreated at 110 °C for 3 h, thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 unit in the air with a heating rate of 10 °C/min.

Structure Determination. A suitable single crystal with dimensions of 0.40 × 0.15 × 0.05 mm^3 was selected for single-crystal XRD analysis. The intensity data were collected on a Rigaku R-AXIS RAPID IP diffractometer [λ(Mo Kα) = 0.71073 Å]. Cell refinement and data reduction were accomplished by the RAPID AUTO program. We solved the crystal structure using direct methods and refined it on F^2 by full-matrix least-squares using the SHELXTL97 software package.[18] The aluminum and phosphorus atoms were determined directly, and then the carbon, nitrogen, and oxygen atoms were found in the difference Fourier map. The hydrogen atoms residing on amine molecules and $PO_2(OH)(=O)$ groups were generated geometrically. Crystal data and details of the data collection are given in Table 1. The selected bond distances for AlPO−CJ21 are presented in Table 2.

Result and Discussion

The diffraction peaks of the powder XRD pattern and the simulated one based on the single-crystal structure analysis are consistent in positions, suggesting the phase purity of the as-synthesized product. The differences in reflection intensity are probably due to preferred orientations in the powder sample (Supporting Information Figure S1)

ICP analysis indicates that AlPO−CJ21 contains Al of 11.64 wt % (calcd 11.45 wt %) and P of 19.52 wt % (calcd 19.72 wt %), which gives rise to the Al/P ratio of 2:3. The elemental analysis shows that the C, H, and N contents are 15.32, 3.95, and 8.86 wt %, respectively, which is consistent with the expected values of 15.29, 3.86 and 8.92 wt %, which are based on the empirical formula given by single-crystal structure analysis.

The TGA in Figure 1 shows a total weight loss of 33.50 wt % from 110 to 1071 °C. The calculated value for the decomposition of the template AEPP is 27.43 wt %. The residual weight loss of 6.07 wt % may be caused by the dehydration of AlPO−CJ21 corresponding to $1.5H_2O$ (calcd 5.74 wt %). XRD studies show that the structure of AlPO−CJ21 collapses above 350 °C, and it transforms to a mixture

Table 1. Crystal Data and Structure Refinement for AlPO−CJ21[a]

empirical formula	$C_6H_{18}Al_2N_3O_{12}P_3$
fw	471.10
T (K)	293(2)
λ (Å)	0.71073
crystal system	monoclinic
space group	$P2_1$
a (Å)	10.069(2)
b (Å)	8.0875(16)
c (Å)	10.598(2)
β (°)	94.71(3)
V (Å^3)	860.1(3)
Z	2
ρ_{calc} (Mg/m^3)	1.819
μ (mm^{-1})	0.516
GOF on F^2	1.036
R [$I > 2\sigma(I)$]	$R_1 = 0.0325$, w$R_2 = 0.0791$
R (all data)	$R_1 = 0.0352$, w$R_2 = 0.0807$
flack parameter	0.03(9)

[a] $R_1 = \sum[\Delta F/\sum(F_o)]$; w$R_2 = \{\sum[w(F_o^2 - F_c^2)]\}/\sum[w(F_o^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o^2)$.

Table 2. Selected Bond Lengths [Å] for AlPO−CJ21[a]

Al(1)−O(2)#1	1.727(2)	P(2)−O(4)	1.5409(19)
Al(1)−O(10)	1.731(2)	P(3)−O(9)	1.505(2)
Al(1)−O(3)#2	1.736(2)	P(3)−O(8)	1.529(2)
Al(1)−O(7)#3	1.744(2)	P(3)−O(6)	1.536(2)
Al(2)−O(8)	1.724(2)	P(3)−O(7)	1.5461(19)
Al(2)−O(6)#3	1.726(2)	C(1)−N(1)	1.472(4)
Al(2)−O(4)	1.737(2)	C(1)−C(2)	1.517(4)
Al(2)−O(12)	1.750(2)	C(2)−N(2)	1.496(4)
P(1)−O(11)	1.499(2)	C(3)−N(2)	1.492(4)
P(1)−O(10)	1.543(2)	C(3)−C(4)	1.521(4)
P(1)−O(12)	1.544(2)	C(4)−N(1)	1.474(3)
P(1)−O(1)	1.567(2)	C(5)−N(1)	1.477(4)
P(2)−O(5)	1.512(2)	C(5)−C(6)	1.519(4)
P(2)−O(2)	1.531(2)	C(6)−N(3)	1.504(4)
P(2)−O(3)	1.540(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1: x, $y + 1$, z; #2: $-x + 1$, $y + 1/2$, $-z$; #3: $-x$, $y + 1/2$, $-z$.

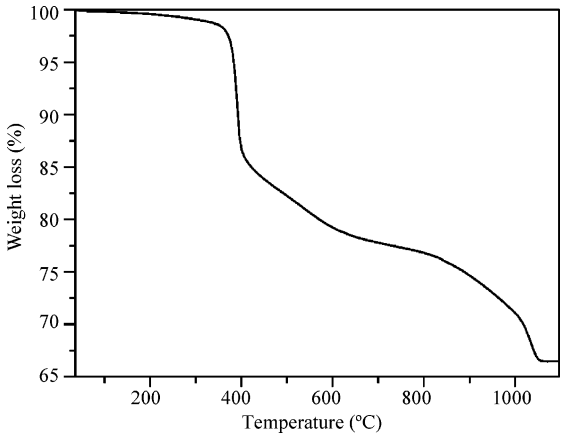

Figure 1. TGA curve of AlPO−CJ21.

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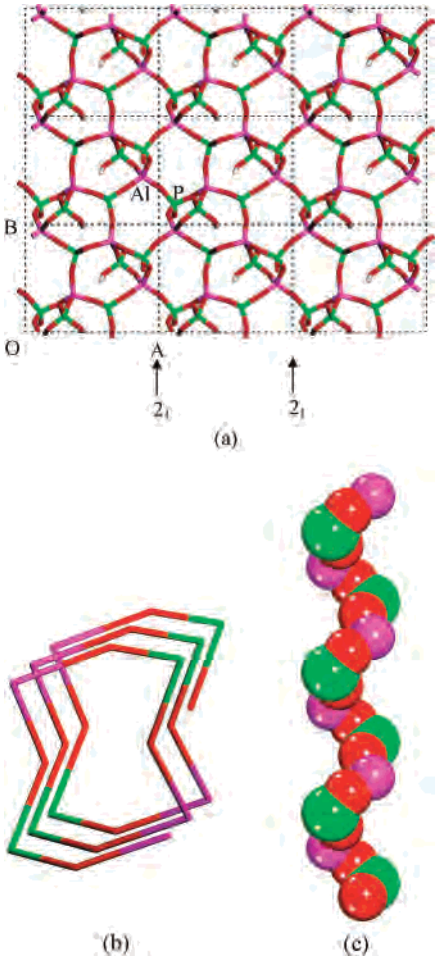

Figure 2. (a) 4.6-net sheet of AlPO−CJ21 parallel to the *ab* plane; (b) the right-handed helical chain following the 2_1 screw axis along the *b* axis; (c) the Corey−Pauling−Koltun (CPK) model of a helical chain.

of $AlPO_4$−tridymite, $AlPO_4$−cristobalite, and $Al_2O_3 \cdot xP_2O_5$ ($x = 1.5$ according to the TGA) above 1000 °C (Supporting Information Figure S2).

The structure of AlPO−CJ21 is composed of macroanionic sheets of $Al_2P_3O_{11}(OH)^{2-}$ and diprotonated AEPP cations located between layers to compensate the negative charges of the inorganic host. Its one asymmetric unit contains two unique Al atoms and three unique P atoms. All Al atoms adopt tetrahedral coordination with typical geometrical parameters [av Al−O, 1.734(2) Å; O−Al−O, 109.43(11)°]. Of the three distinct P atoms, P(1) shares two O atoms with adjacent Al atoms [av P(1)−O, 1.543(2) Å] and has one terminal P−OH group [P(1)−O(1), 1.567(2) Å] and one terminal P═O group [P(1)−O(11), 1.499(2) Å]. P(2) and P(3) each make three P−O−Al bonds [av P−O, 1.536(2) Å], leaving one terminal P═O group [av P═O, 1.508(2) Å].

As seen in Figure 2, the alternation of AlO_4 and PO_3(═O)/PO_2(OH)(═O) tetrahedra forms a new type of 4.6-net sheet parallel to the *ab* plane, which contains right-handed helical chains following a 2_1 screw axis running along the *b* axis. The inorganic sheets can also be viewed as comprising rows of edge-sharing 6MRs bridged by 2-connected PO_2-(OH)(═O) groups alternatively above and below the sheet. This structural character of bridged 6MRs acting as a second building unit (SBU) has been commonly observed in the

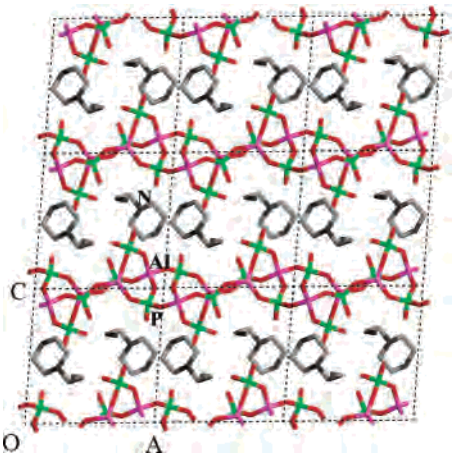

Figure 3. Crystal structure of AlPO−CJ21 viewed along the [010] direction (H atoms of template are omitted for clarity).

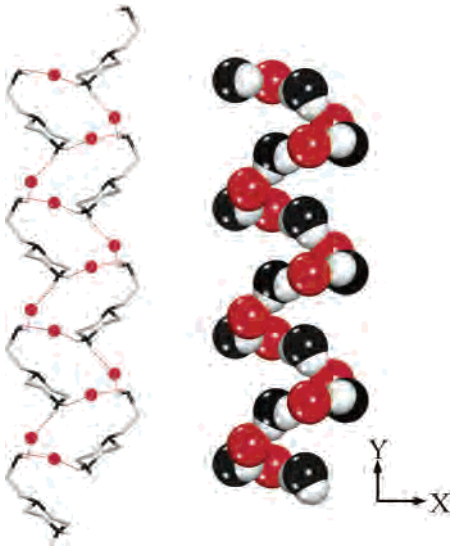

Figure 4. View of a right-handed hydrogen-bonded helical chain formed by the templates and the inorganic layers along the *b* axis (figure on the right is CPK model; H atoms of carbon are omitted for clarity). O, red; C, gray; H, white; N, black.

reported layered aluminophosphates with $Al_2P_3O_{12}^{3-}$ stoichiometry.[6−9] It is noted that this 4.6-net sheet was previously predicted as a hypothetical network of $Al_2P_3O_{12}^{3-}$ stoichiometry by Yu and Xu et al. on the basis of the construction of $Al_2P_3O_{12}^{3-}$ layers from SBUs.[9] However, the 2D layered structure with this sheet had not been prepared until now.

The 4.6-net porous sheets stack in an AAAA sequence along the *c* direction (Figure 3). One very strong interlayer hydrogen bond is formed between the P═O(5) and P−O(1)H groups, characterized by a O(5)···O(1) distance of 2.554(3) Å. Extensively strong hydrogen bonds are formed between the inorganic hosts and the organic AEPP cations. One $-N(3)H_3^+$ group of AEPP is hydrogen-bonded to two terminal O atoms of one sheet [N(3)···O(5), 2.857(3) Å; N(3)···O(9), 2.716(3) Å] and one terminal O(11) atom of another sheet [N(3)···O(11), 2.857(3) Å]. The N(2) atom in the ring forms two hydrogen bonds with the terminal O(9) and O(11) atoms in the same layer [N(2)···O(9), 2.728(3) Å; N(2)···O(11), 2.766(3) Å]. Fascinatingly, the diprotonated

AEPP cations arrange between layers in an unusual manner, which leads to zigzag-like hydrogen-bonded helices following the 2_1 screw axes along the *b* axis. These hydrogen-bonded helices of host−guest systems are exclusively right-handed and are consistent with the right-handed inorganic helical chains that exist in 4.6-net sheets. Furthermore, the left-handed inorganic helical chains and hydrogen-bonded helices of host−guest systems are found in another crystal selected with a space group of $P2_1$. This indicates that each single crystal of AlPO−CJ21 is chiral, and the bulk product should be a 50:50 mixture of enantiomers exhibiting a racemic character.

Figure 4 shows a view of a right-handed hydrogen-bonded helix formed between the organic templates and the inorganic sheets. The hydrogen-bonded helices are observed in a variety of supramolecular assembly materials[14,15,19−21] but are particularly rare in the organically templated aluminophosphates.

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Conclusion

A new layered aluminophosphate $[C_6N_3H_{17}][Al_2(HPO_4)(PO_4)_2]$ with unique 4.6-net sheets has been synthesized in a solvothermal system. Its inorganic sheets built up from AlO_4, $PO_2(OH)(=O)$, and $PO_3(=O)$ tetrahedra contain right- or left-handed helical chains following 2_1 screw axes. The sheets are held together by the diprotonated AEPP cations located between the layers through hydrogen bonds. Strikingly, right- or left-handed hydrogen-bonded helices are self-assembled between inorganic sheets and organic AEPP cations in the host−guest system.

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Supporting Information Available: XRD pattern of as-synthesized AlPO−CJ21 compared with the simulated one based on the single-crystal structure analysis and XRD pattern of the product heated at 1000 °C for 3 h. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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