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Supporting information

A Highly Porous Three-dimensional Aluminum Phosphonate with Hexagonal Channels: Synthesis, Structure and Adsorption Properties

Si-Fu Tang, Jin-Jun Cai, Liang-Jun Li, Xiao-Xia Lv, Chao Wang and Xue-Bo Zhao

Materials and Instruments.

All chemicals were obtained from commercial sources and used without further purification. The synthesis of (2,4,6-trimethylbenzene-1,3,5-triyl) tris(methylene)triphosphonic acid (H_6L) was reported elsewhere.[1] Elemental analyses were performed on a Vario EL III elemental analyzer. IR spectra were recorded on a Nicolet 6700 FTIR Spectrometer as KBr pellets in the range of 4000-400 cm^{-1}. Powder X-ray patterns were obtained on a Bruker D8 Advance diffractometer using CuKα radiation. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10 °C/min under a nitrogen atmosphere. Gas adsorption isotherms of H_2, N_2, and CO_2 were measured by using an Intelligent Gravimetric Analyzer (IGA) from Hiden (Hiden Isochema, Warrington, UK). This apparatus is an ultrahigh vacuum, clean system with a diaphragm and turbo pumping system,[2] which allows isotherms and the corresponding kinetics of adsorption and desorption to be determined for set pressure steps.

Single-Crystal Structure Determination.

Single crystal X-ray diffraction measurements of compound **1** was carried out on a Bruker SMART APEX II CCD diffractometer (Mo Kα radiation, λ= 71.073 pm) at room temperature. SAINT was used for integration of intensity of reflections and scaling.[3] Absorption corrections were carried out with the program SADABS.[4] Crystal structures were solved by direct methods using SHELXS.[5] Subsequent difference Fourier analyses and least squares refinement with SHELXL-97[6] allowed for the location of the atom positions. In the final step of the crystal structure refinement hydrogen atoms of idealized $–CH_2$ and $–CH_3$ groups were added and treated with the riding atom mode, their isotropic displacement factor was chosen as 1.2 and 1.5 times the preceding carbon atom, respectively. The hydrogen atoms on the water molecule were located from the difference Fourier map. The crystallographic details for compound **1** are summarized in Table S1. The data have been deposited in the Cambridge Crystallographic Data Centre (CCDC), deposition number CCDC 969636 for compound **1**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

[1] S.-F. Tang, X.-B. Pan, X.-X. Lv, S.-H. Yan, X.-R. Xu, L.-J. Li, X.-B. Zhao, *CrystEngComm*, 2013, **15**, 1860–1873.

[2] M. J. Benham, D. K. Ross, *Z. Phys. Chem. Neue Folge* 1989, **163**, 25-34.

[3] SAINT, Version 6.45; Bruker Analytical X-ray Systems Inc.: 2003.

[4] G. M. Sheldrick, SADABS, Version 2.10; Bruker AXS Inc.: Madison, WI, 2003.

[5] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, 1997.

[6] G. M. Sheldrick, *SHELXTL*, *Crystallographic Software Package*, SHELXTL, Version 5.1, Bruker-AXS, Madison,WI, **1998**.

Table S1. Crystallographic and refinement data of compound **1**.

compound	**1**
formula	$C_{12}H_{20}AlO_{10}P_3$
fw	444.17
space group	*R*-3
a (Å)	35.285(3)
b (Å)	35.285(3)
c (Å)	12.398(3)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	13367(3)
Z	18
D_{calcd}, (g cm^{-3})	0.993
abs coeff (mm^{-1})	0.260
reflns collected	10451
independent reflns/R_{int}	5187 / 0.0611
GOF on F^2	0.998
final R indices [I>2σ(I)]: R_1, wR_2 ^{a}	0.0567, 0.1223
R indices (all data): R_1, wR_2	0.1184, 0.1495

Table 2. Selected bond lengths of compound **1**.

Al(1)-O(9)	1.841(3)	Al(1)-O(6)#2	1.878(3)
Al(1)-O(8)#1	1.848(3)	Al(1)-O(3)#3	1.942(3)
Al(1)-O(2)	1.857(3)	Al(1)-O(1W)	1.999(3)
O(1)-P(1)	1.558(3)	O(7)-P(3)	1.557(3)
O(2)-P(1)	1.500(3)	O(8)-P(3)	1.499(3)
O(3)-P(1)	1.511(3)	O(9)-P(3)	1.491(3)
O(4)-P(2)	1.534(3)	P(1)-C(7)	1.803(4)
O(5)-P(2)	1.551(3)	P(2)-C(9)	1.797(4)
O(6)-P(2)	1.487(3)	P(3)-C(11)	1.808(4)

Symmetry transformations used to generate equivalent atoms: #1 -y+2/3, x-y+4/3, z+1/3; #2 -x+1/3, -y+5/3, -z+2/3; #3 -x+y-2/3, -x+2/3, z-1/3.

Table S3. Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H···A	D···A	<(DHA)	
0.82	1.78	2.585(4)	168.4	O1-H1A···O4_$1
0.82	1.70	2.504(4)	165.4	O5-H5A···O4_$1
0.82	1.81	2.627(4)	171.8	O7-H7C···O5_$1
0.85	2.53	3.210(4)	138.0	O1W-H2W···O2_$2
0.85	2.05	2.818(4)	149.9	O1W-H2W···O3_$3

Operators for generating equivalent atoms: $1 -x+1/3, -y+5/3, -z+2/3; $2 -x+y-2/3, -x+2/3, z-1/3; $3 -y+2/3, x-y+4/3, z-2/3.

Synthesis of compound Al(H_3L)(H_2O) (1)

A mixture of H_6L (0.2 mmol, 0.0841 g), $Al_2(SO_4)_3\cdot18H_2O$ (0.125 mmol, 0.0833 g), 9 mL ethanol and 1 mL of water were placed and stirred in a Teflon-lined autoclave. Afterward, it was sealed and heated at 140 ^{o}C for 3 days and allowed to cool to room temperature in a time period of 24 hours. Colorless cubic crystals (0.078 g, 88%, based on ligand) were collected and washed with deionized water. Elemental analysis (%) calcd for $C_{12}H_{20}AlO_{10}P_3$ (444.17): C 32.45, H 4.54; found: C 28.71, H 4.83. The large discrepancy indicates the existence of plenty of guest molecules (probably three water molecules in each formula; calcd: C 28.93 %, H 5.26 %.). IR (KBr, cm^{-1}): 3423.5 (vs), 2348.0 (m), 1636.8 (s), 1474.0 (w), 1427.9 (w), 1378.4 (w), 1231.2 (m), 1154.6 (s), 1050.8 (s), 957.4 (m), 783.3 (w), 747.9 (w), 640.4 (w), 499.4 (m), 440.3 (m).

Neither pure ethanol nor water produces crystalline product. Different ligand/metal molar ratios and temperatures were also scanned to find the most optimised synthesis condition. It was found a ligand/metal molar ratio of 0.8 and 140 ^{o}C was the best synthesis condition to get the most optimising yield and crystal size.

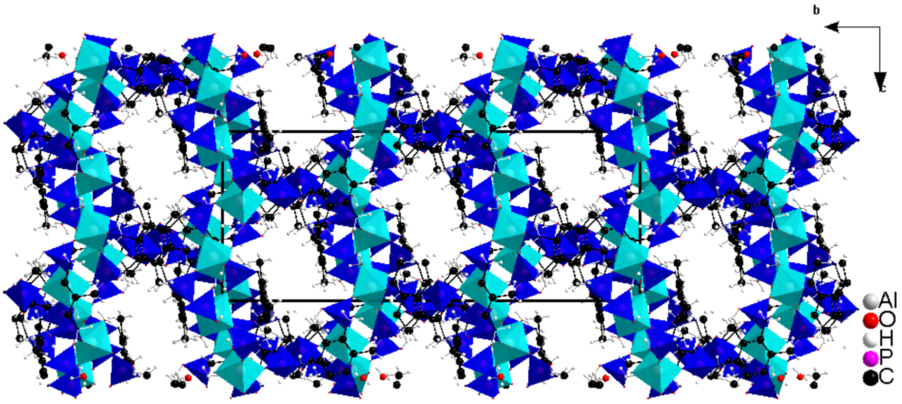


Figure S1. Three-dimensional framework structure along *a*-direction in compound **1**. The AlO_6 octahedra and $–CPO_3$ tetrahedrons are shaded in cyan and blue, respectively.

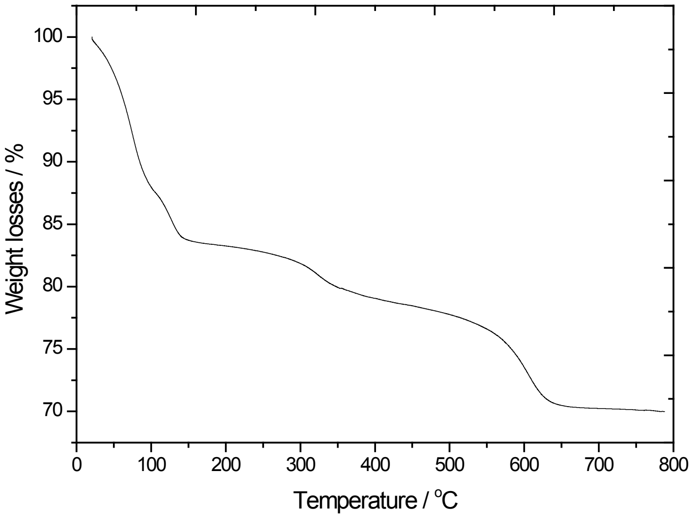


Figure S2. TGA diagram of compound **1**.

Thermalgravimetric analysis was performed in the temperature range of 30-900 ^{o}C to examine the thermal stability of the title compound. It started to lose weight immediately upon heating. The first weight loss (observed: 16.43 %) from room temperature to 160 ^{o}C could be ascribed to the losses of guest molecules indicating the presence of H_2O/ethanol molecules accommodated in the channels. Then the weight loss slowed down to reach a plateau which was followed by the second (200-370 ^{o}C) and third weight (500-650 ^{o}C) losses. The second weight loss could be ascribed to the removal of the coordinated water molecule (calcd: 4.05 %; observed:

4.02 %), whereas the third one should be caused by the collapse of the framework.

Calculation of Langmuir surface area:

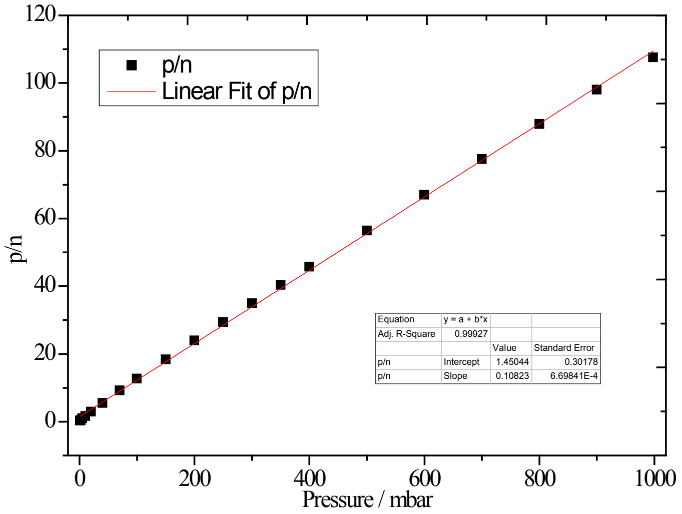


Figure S3. Langmuir graph for N_2 adsorption on **1** at 77 K.

The isotherms of N2 at 77 K were fitted using the Langmuir equation (as shown in equation 1):

$$\frac{P}{n} = \frac{P}{n_m} + \frac{1}{bn_m} \quad (1)$$

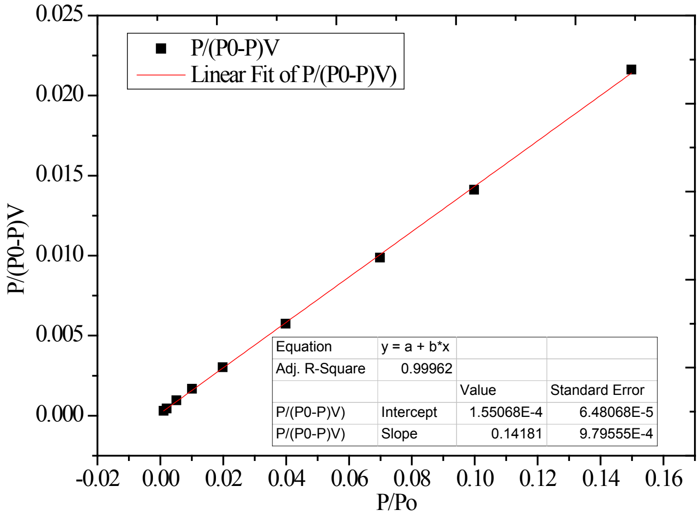
Where p is the pressure, n is the amount adsorbed, n_m is the monolayer capacity, and b is the coefficient of adsorption related to the adsorbate/adsorbent system. The slope of the fitted line for the Langmuir equation is 0.10823, which is equal to $1/\mathrm{n_m}$.

$\mathrm{n_m} = 1/0.10823 = 9.24\ \mathrm{mmol\cdot g^{-1}}$

The Langmuir surface area is calculated by the following equation.

$\mathrm{Sg} = \mathrm{n_m \cdot A \cdot \sigma_m} = 9.24\times10^{-3}\times6.023\times10^{23}\times1.62\times10^{19} = 901.5\ \mathrm{m^2\cdot g^{-1}}$

Calculation of BET surface area:



Equation	y = a + b*x		
Adj. R-Square	0.99962		
		Value	Standard Error
P/(P0-P)V)	Intercept	1.55068E-4	6.48068E-5
P/(P0-P)V)	Slope	0.14181	9.79555E-4

Figure S4. BET plot of **1** for N_2 adsorption at 77 K.

The BET surface area of compound **1** was calculated by using Brunauer-Emmett-Teller equation from N_2 adsorption isotherm at 77 K (as shown in equation 2).

$$\frac{P}{V(P_o-P)} = \frac{1}{CV_m} + \frac{C-1}{CV_m}\frac{P}{P_o} \qquad (2)$$

Using the N_2 isotherm of compound **1** at 77 K, the term $P/V(P_0\text{-}P)$ was plotted and linear fitted with P/P_0 in the pressure range of $0 < P/P_0 < 0.15$, as shown in Fig. S4. According to the Brunauer-Emmett-Teller equation, the term $(C\text{-}1)/\ CV_m$ and $1/CV_m$ are equal to the slope and the intercept of the fitted line, respectively.

$(C\text{-}1)/V_m= 0.14181$

$1/(CV_m)=1.55\times10^{-4}$

So, we can obtain the value of C and V_m for compound **1** as following:

C= 916

$V_m= 7.043\ \mathrm{mmol\cdot g^{-1}}$

The BET surface area is calculated by the equation 3.

$S_{BET}= V_m\cdot A\cdot\sigma_m$ (3)

Where A is the Avogadro constant ($6.023\times10^{23}\ \mathrm{mol^{-1}}$), *m* is sectional area of one nitrogen molecular (1.62×10^{-19} m^2). So the BET surface area of compound **1** is 687.2 m^2 /g.

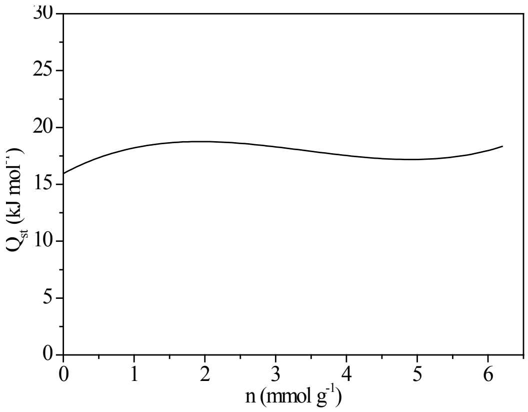


Figure S5. Isosteric adsorption enthalpies of CO_2 on activated **1**.