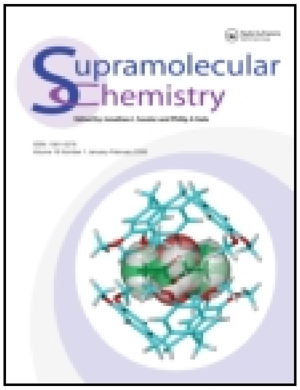

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Ramanathan Vaidhyanathan [a] , Junmei Liang [a] , Simon S. Iremonger [a] & George K.H. Shimizu [a]

[a] Department of Chemistry, University of Calgary, Calgary, Alberta, Canada

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A route to functionalised pores in coordination polymers via mixed phosphonate and amino-triazole linkers

Ramanathan Vaidhyanathan, Junmei Liang, Simon S. Iremonger and George K.H. Shimizu*

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada

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The ability to control size, shape and functionality of pores in materials is of fundamental importance to understanding sorption (host–guest) phenomena. We present a coordination polymer compound with narrow pores lined by free amine functionalities. Cu(aminotriazole)(1,4-dihydrogenphosphonate)hydrate, **1**, forms a pillared layered structure where alternating pillaring units are replaced by the N-heterocycle to generate the pores. Single-crystal and powder X-ray diffraction data are presented as well as the thermogravimetric analysis and CO_2, N_2 and H_2 gas sorption analyses.

Keywords: coordination polymer; phosphonate; triazole; metal organic framework; copper

Introduction

The ability to line the pores of a framework solid with specific chemical functionalities, along with the size and shape of the pore itself, is fundamental to controlling the host–guest chemistry of the network. Porous coordination polymers/metal organic frameworks are known for their crystallinity that imparts well-defined porosity and regular sorption properties (*1*). Recently, approaches to control the chemical functionality of lining pores have received much attention. This can be either by direct lining of pores with functional groups (*2*) or by post-synthetic modification of the networks (*3*). The interest in lining pores with amine groups stems from a physisorption perspective (*4*), in the polar nature of the functional group which can induce higher polarisation of guest molecules and, from a chemisorptive standpoint (*5*), from their well-established carbamate formation with CO_2 exploited in industrial CO_2 scrubbing (*6*). For practical gas storage/separations, another key factor is framework stability, not just thermal but hydrolytic stability as many target gas streams would contain water at some level (*7*).

Two ligands that have been studied for the formation of porous coordination frameworks are phosphonates (*8*) and triazolates (*9*). Organophosphonates (RPO_3^{2-}), with simple linear spacers, have a tendency to form dense solids where the organic pendants pack to form a hydrophobic interlayer. This also extends to linear diphosphonate and dihydrogenphosphonate ligands. Triazolates, akin to the imidazolates (*10*) employed for zeolitic imidazolate frameworks (*11*), tend to bridge three metal ions into a network structure. As the neutral triazole molecule, the typically observed ligation is only through two N atoms in a bidentate bridging mode (*12*).

Here, we present a new pillared layered architecture, Cu(HL1)(H_2L2), **1**, where HL1 = neutral 3-amino-1,2,4-triazole and H_2L2 = dianionic 1,4-benzenedihydrogenphosphonate. The key features demonstrated by this material are the fact that the pillars no longer pack in a dense fashion owing to the hybrid inorganic–organic structure being interspersed by aminotriazole units. Pores could be formed via an approach that could be generalised to a family with other linear phosphonates. Also, the amine functionalities of the aminotriazole molecules point into the prospective voids, which is germane to CO_2 capture.

Experimental

Synthesis

All reagents were obtained from Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada) and used without further purification. Benzene-1,4-diphosphonic acid was prepared by using a procedure reported in the literature (*13*).

*Synthesis of Cu(HL1)(H_2L2)·(H_2O)$_2$ (**1**)*

Rod-shaped green single crystals of **1** were obtained from the reaction of a mixture containing $CuCO_3·Cu(OH)_2$ (0.06 g, 0.27 mmol), $C_6H_4(PO_3H_2)_2·(H_2O)$ (0.05 g, 0.195 mmol), 3-amino-1,2,4-triazole (0.18 g, 2.1 mmol), methanol (2 ml) and water (2 ml) at 150°C for 2 days. A yield of ~55% was obtained in this reaction (calculated with respect to the H_2L2). Polycrystalline **1** could be obtained in bulk as follows: $CuCO_3·Cu(OH)_2$ (0.10 g,

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*Corresponding author. Email: gshimizu@ucalgary.ca

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0.45 mmol) was dispersed in water (25 ml) along with $C_6H_4(PO_3H_2)_2{\cdot}(H_2O)$ (0.116 g, 0.45 mmol) and 3-amino-1,2,4-triazole (0.084 g, 1 mmol). The mixture was refluxed at 100°C for 16 h to obtain a green-coloured polycrystalline sample of **1**$\cdot(H_2O)_2$. A yield of ~85% was obtained from this reaction (calculated with respect to H_2L2). The powder X-ray diffraction pattern of this sample matched well with the pattern simulated from the single-crystal X-ray diffraction data. CHN values for $Cu_2(C_6H_4(PO_3H)_2)_2(C_2H_4N_4)_2{\cdot}(H_2O)_3$ (calculated within brackets): C 23.39 (23.40); H 3.26 (3.19); N 13.38 (13.64)%.

Single-crystal data collection

The CIF file for **1** has been deposited with CCDC registry number 784367. Single crystals were mounted by freezing to the tip of a glass capillary using Paratone oil. Experiments were conducted at 173 K on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (= 0.71069 Å) and equipped with a CCD detector. The intensity data collection was performed in the α-ϕ scanning mode with the goniometer and detector angular settings optimised using the program COLLECT (Bruker AXS BV, Madison, WI, USA; 1997–2004). The crystal-to-detector distance was 30 mm. The unit cell and the orientation matrix were refined using the entire data-set of reflections. The diffraction spots were measured in full with a high accuracy, scaled with SCALEPACK (*14*) corrected for Lorentz-polarisation correction, and integrated using DENZO (*14*). Absorption effects were empirically corrected by Gaussian quadrature using Sortav. Full-matrix least-squares refinement on F^2 was carried out using SHELXL97 (*15*).

Thermal analysis

Thermogravimetric analysis and differential scanning calorimetry data were recorded on a Netzsch STA 449C apparatus with a heating rate of 5°C/min in the temperature range of 30–450°C under N_2 atmosphere.

Gas sorption analysis

Adsorption isotherms for CO_2 (99.998%), N_2 (99.999%) and H_2 (99.999%) were conducted using an Accelerated Surface Area & Porosimetry System 2020 supplied by Micromeritics Instruments Inc. (Norcross, GA, USA). In a general procedure, the dry sample (~100 mg) was loaded into the glass analysis tube. The sample was heated under vacuum (~10^3 mbar) in two stages, initially to 60°C at 1°C/min for 1 h and then to 80°C at 1°C/min for 3 h. After this, the outgas rate was less than 2 μbar/h. The sample was then backfilled with N_2 before being transferred to the analysis port where it was evacuated for a further 3 h before the analysis was started.

Results and discussion

Compound **1** was successfully prepared in both single crystal and bulk forms. Rod-shaped green single crystals of **1** were obtained from the solvothermal reaction of $CuCO_3{\cdot}Cu(OH)_2$ (0.27 mmol), H_4L2 (0.195 mmol) and HL1 (2.1 mmol) in 4 ml of 1:1 methanol/water at 150°C for 2 days. Compound **1** could be prepared in bulk by refluxing a 1:2.2:1 molar ratio of $CuCO_3{\cdot}Cu(OH)_2$:HL1:H_4L2 in water for 16 h.

The single-crystal structure of compound **1** shows a network with one-dimensional (1D) pores running down the *a*-axis, as shown in Figure 1(a),(b). The structure can be described as 1D columns of six-coordinate Cu^{2+} ions that are bridged by both HL1 and H_2L2 ligands. The HL1

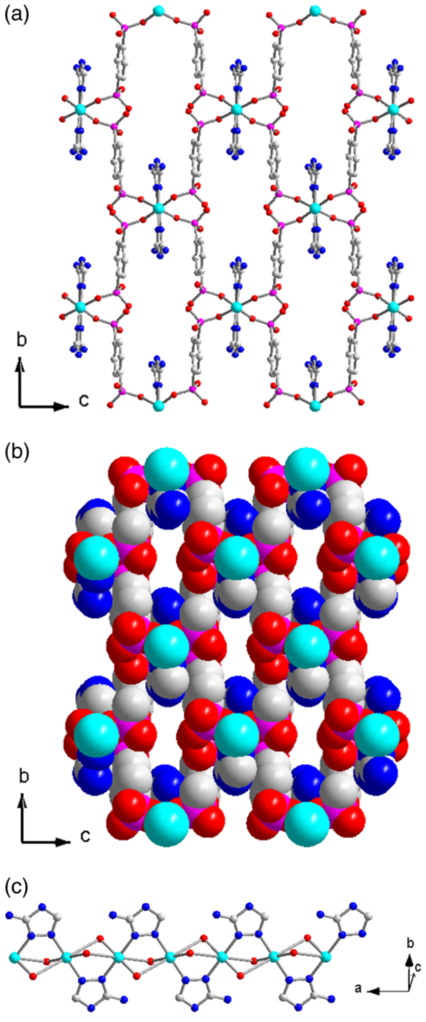

Figure 1. Structure of **1**. Colours: Cu, cyan; P, pink; O, red; C, grey. (a) Ball and stick representation showing amine groups lining the pores. (b) Space-filling representation. (c) One of the HL1-bridged Cu columns running along the *a*-axis.

ligands coordinate in a bidentate fashion bridging two Cu centres (Cu1—N2 = 1.978(2) Å, Cu2—N1 = 1.983(2) Å), as shown in Figure 1(c). The Cu coordination spheres are completed by four phosphonate oxygen atoms, a single donor from four different RPO_3H^- groups, and are tetragonally distorted (Cu1—O3 = 1.963(2) Å, Cu1—O4 = 2.826(2) Å, Cu2—O3 = 2.725(2) Å, Cu2—O4 = 1.972(2) Å). Thus, each Cu centre bridges four different H_2L2 ligands in the *bc* plane. These layers are then bridged down the *a*-direction by the HL1 molecules and the HL1 molecules form the upper and lower edges of the pores. In addition to the Cu ligation, the HL1 molecules are further stabilised by two sets of π-stacking interactions with the phenyl rings of neighbouring H_2L2 molecules (perpendicular mean plane distance between the triazole ring of L1 and the phenyl ring of L2 = 3.28(1) Å). There are apparent void spaces in the structure which measure 4.1 × 8.9 Å, excluding van der Walls radii. Notably, the amine groups of the HL1 molecules line the tops and bottoms of the pores. The HL1 molecules are twofold disordered and so each C site is functionalised with a 50% occupied amine group. Given the interest in using amine-lined porous compounds for CO_2 sorption, this observation is significant.

The term 'apparent' has been used to describe the pores in compound **1** as the true measure of porosity would be the accessibility of the solid's interior to a fluid or gaseous phase. The thermogram of **1** (Figure 2(a)) shows two mass losses, from 50 to 105°C and from 160 to 203°C, each corresponding to the loss of **1** water molecule per formula unit (calculated = 4.3% for $\mathbf{1}\cdot(H_2O)_2$, observed = 4.1 and 4.3%). Above 203°C, another mass loss begins that continues steadily to the upper temperature limit of the analysis (450°C). This mass loss, ~16%, is almost certainly the loss of HL1 molecules from the structure as they are the only other neutral component. Complete loss of HL1 would correspond to a 21.9% mass loss. Gas sorption measurements (Figure 2(b)) were conducted on compound **1** with N_2 and H_2 at 77 K and CO_2 at 273 K The activation of the pores was done at 80°C and $\sim 10^{-3}$ mbar pressure, conditions which should not remove HL1 from the structure. At 77 K, **1** shows no appreciable adsorption of N_2 or H_2. However, at 273 K, a small amount of CO_2 (0.5 mmol/g) was adsorbed. Fitting of the CO_2 isotherm to the BET model gave a surface area of 69 m^2/g. A look at the thermogravimetric analysis of **1** shows three distinct stages of mass loss. Although no water molecules were located in the single-crystal structure of **1**, it would be reasonable to expect atmospheric water to be adsorbed into the pores. The comparatively minor gas uptake in this material is likely to arise from the partial collapse of the network upon the dehydration of the network. As the pores in the material are 1D even a small degree of collapse would significantly reduce the accessible void space. Indeed, the 273 K CO_2 isotherm shows a significant degree of hysteresis which would indicate that a kinetic barriers to gas

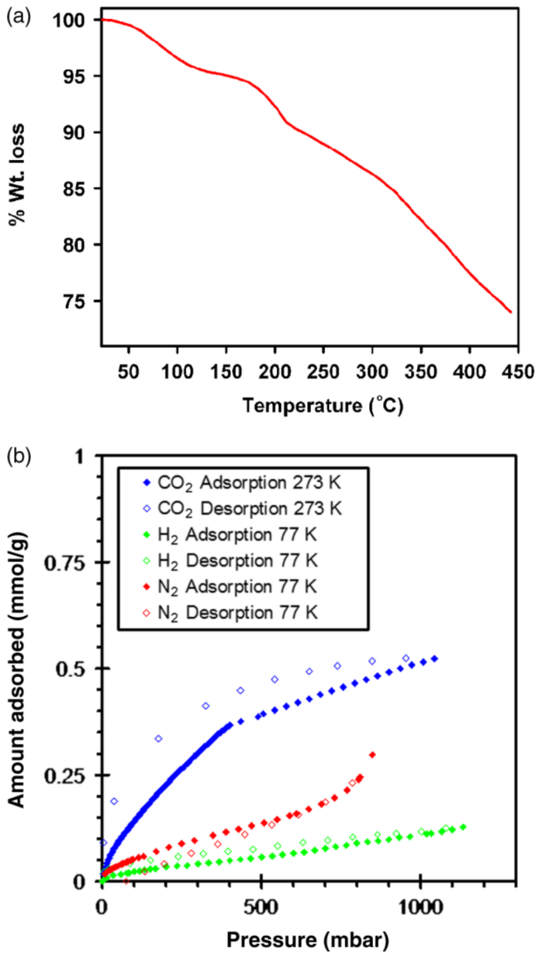

Figure 2. (a) Thermogram of **1** showing two-stage loss of water and then HL1 over 200°C. (b) Gas sorption analysis of **1**. Note the hysteresis in the CO_2 desorption.

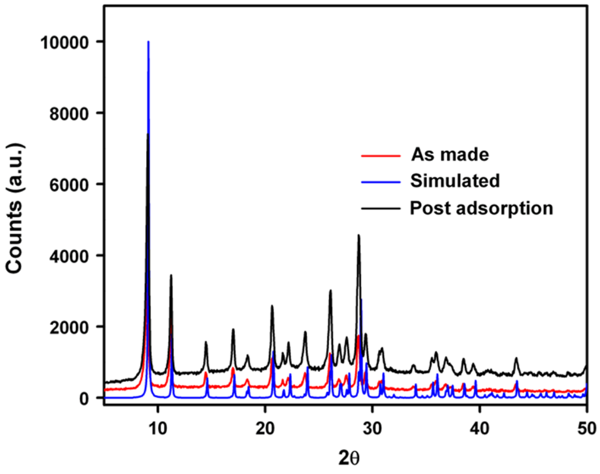

Figure 3. Powder X-ray diffraction patterns of **1** comparing the single-crystal phase (simulated), the bulk phase (as made) and the bulk phase post gas sorption showing structure retention.

diffusion exists in the structure. Powder X-ray diffraction studies (Figure 3) showed that the sample, after activation and gas sorption analysis, retained its structure and that the HL1 molecules were not being removed in the activation process. In any event, the true value of compound **1** rests more as a basis for the design of other porous coordination polymers more so than the presently observed properties.

The structure of **1** is best considered in comparison to the structure of $Cu(H_2L2)\cdot(H_2O)$, **2**, reported by Clearfield (*16*), so a brief description of **2** will be provided. Compound **2** forms the classic hybrid inorganic–organic layered structure where (hydrogen) phosphonate groups bridged metal ions into layers (Figure 4). The layers have pendant organic groups projected in the perpendicular direction which serve to define a hydrophobic interlayer region. If the organic pendants are difunctional, they act as true 'pillars' and connect the layers in the third dimension. Unfortunately, this highly stable configuration results in pendant groups that are typically efficiently packed rendering the interlayer space inaccessible to external guest molecules. Approaches to rectify this have typically employed the insertion of either phosphate or smaller organophosphonate groups into the layer structure to increase separation between pillars and generate void space (*17*). The main shortcoming with this strategy is that the pillars are not dispersed with long-range order and these materials lack crystallinity. Using wider pillars on a simple diphosphonate backbone can also give open structures (*18*). The structure of **1** bears an interesting correlation with that of compound **2** and this correlation is the basis of a design paradigm. The structure of compound **1** can be viewed as arising from the replacement of entire rows of $Cu(H_2L2)$ columns from the structure of compound **2** with columns of HL1 molecules. In relation to Figure 1, the columns labelled A–E could be 'removed' to leave unsaturated Cu centres in the regions adjacent to the created virtual void. Insertion of HL1 molecules would provide the necessary ligation to complete the Cu coordination spheres and stabilise the 3D structure. This relationship between the two structures is offered merely to illustrate the common elements between dense compound **2** and open structure **1**. As mentioned, with linear diphosphonate ligands, often a dense structure represents the thermodynamic minimum. A key attribute of **2** is the presence of a coordinated water molecule on the Cu centre. This indicates the packing of the $Cu—RPO_3H$ layers and the interlayer organic groups are not ideally commensurate and that the system is predisposed to additional ligation (*19*). It is also apparent though that the analogous reaction performed with 4,4′-biphenyldiphosphonic acid could likely yield a structure with larger amine-lined pores. Longer narrow pores have been evoked as promising not for storage of gases but for very selective separations (*20*).

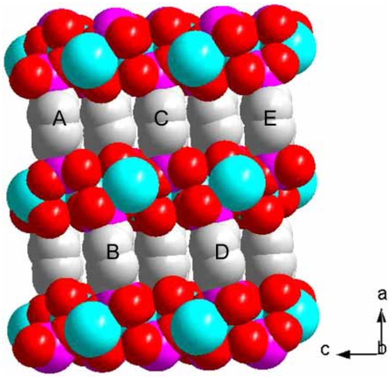

Figure 4. Structure of **2**, Cu(1,4-benzenedihydrogen phosphonate)hydrate, $Cu(H_2L2)\cdot(H_2O)$ as determined from powder X-ray diffraction showing the prototypical hybrid inorganic–organic layer motif. The labels A–E are for comparison to **1**. Colours: Cu, cyan; P, pink; O, red; C, grey.

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