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A Robust Metal–Organic Framework Constructed from Alkoxo-Bridged Binuclear Nodes and Hexamethylenetetramine Spacers: Crystal Structure and Sorption Studies

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Supporting Information

ABSTRACT: A neutral 3D metal–organic framework, ${}^3_\infty[Cu_2(mand)_2(hmt)]\cdot H_2O$ (**1**), was constructed from binuclear Cu_2O_2 alkoxo-bridged nodes, generated by the doubly deprotonated mandelic acid. The nodes are connected by hexamethylenetetramine (hmt) spacers, which act as biconnective bridging ligands, and by carboxylato groups. Channels are observed along the crystallographic *c* axis. The water molecules from the channels can be easily removed, preserving the architecture of the crystal, which is stable up to 280 °C. The Langmuir surface area was found to be 610 $m^2\ g^{-1}$. The sorption ability of **1** was investigated using H_2 and CO_2.

The construction of molecular crystals featuring nanosized cavities or channels represents one of the hottest topics in crystal engineering and materials science.[1] It was already reported that the coordination polymers may have potential applications in various fields: catalysis,[2] molecular magnetism and multifunctional molecule-based materials,[3] separation and storage of specific molecules,[4a−f] and even bioactive molecules.[4g] The packing of coordination networks generates voids, cavities, or channels, which may account for more than half of the crystal volume.[5] A major factor to be considered for solids is the tendency to minimize void space within their structures. The empty space resulting from the packing of coordination polymers can be filled by (1) hosting the anions, solvent molecules, and uncoordinated ligand molecules and (2) interpenetration, that is, the voids associated with one framework are occupied by one or more independent frameworks. For catalytic or sorption applications, the molecular crystals must be porous. In order to construct them, anionic spacers or anionic ancillary ligands are the most appropriate.

In a series of papers, some of us have shown that amino alcohols generate spontaneously binuclear alkoxo-bridged cationic species, which can act as nodes in constructing mono- and bidimensional coordination polymers.[6] Aiming to obtain neutral coordination networks and taking advantage of the ability of the alkoxo group to generate binuclear nodes, we decided to employ a hydroxy acid, the mandelic acid (H_2mand), which can acts as a dianionic ligand (Chart S1 in the Supporting Information, SI).[7] As a spacer, we have chosen a very common organic molecule, hexamethylenetetramine (hmt), which is known to be a versatile tecton in crystal engineering.[8]

The reaction between copper(II) perchlorate, DL-mandelic acid, and hmt in the presence of triethylamine and ammonia leads to a highly crystalline material: ${}^3_\infty[Cu_2(mand)_2(hmt)]\cdot H_2O$ (**1**; see the SI). The crystal structure of **1** (see the SI) has been solved and consists of a neutral 3D coordination network (Figure 1).

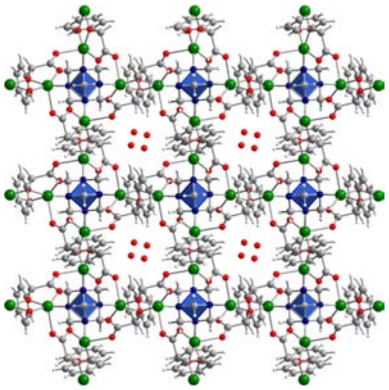

Figure 1. Crystal structure of **1**. View along the channels, which follow the crystallographic *c* axis. The hmt molecules are highlighted in blue.

As expected, the neutral alkoxo-bridged binuclear nodes, $\{Cu_2(mand)_2\}$, are self-assembled into a supramolecular network (Figure 2). The copper atoms are crystallographically equivalent, and the three-dimensional development of the coordination polymer is quite interesting. First of all, we notice that the carboxylato group is connected through its oxygen atoms to two copper ions: one oxygen atom (O1) chelates, together with the alkoxo oxygen (O3) atom, the copper ion,

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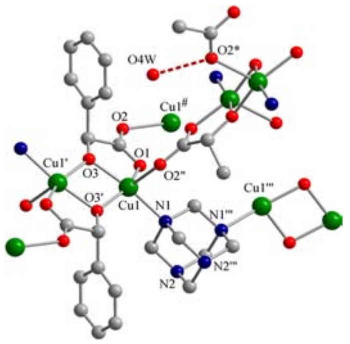

Figure 2. Perspective view of a binuclear node and its connectivities to neighboring nodes, along with the atom numbering scheme.

and the other one (O2) is coordinated to the copper ion from another node (syn−anti bridging mode). The intranode distance between the copper ions is 3.0017(6) Å. Each cooper ion is pentacoordinated, with a slightly distorted square-pyramidal geometry, with the apical position being occupied by the oxygen atom belonging to the carboxylato group of a neighboring node (Cu1−O2″ = 2.314(2) Å, where ″ = 1.25 − *y*, 0.25 + *x*, 0.25 − *z*). The basal plane is formed by one carboxylato, two alkoxo oxygen atoms, and a nitrogen atom from the hmt ligand (Cu1−O1 = 1.9500(19) Å; Cu1−O3 = 1.9351(17) Å; Cu1−O3′ = 1.9616(17) Å; Cu1−N1 = 2.0514(19) Å, where ′ = 1 − *x*, 2 − *y*, −*z*). The hmt molecule acts as a bridge through two out of the four nitrogen atoms, resulting in chains (Figures 2 and 3a), which run in perpendicular planes. The connections between the neighboring perpendicular {Cu_2(hmt)} chains are made by the carboxylato groups (Figures 2 and 3b−d). The distance between the copper ions bridged by the carboxylato group is 5.431 Å, while the one between the copper ions connected by the hmt bridge is 5.761 Å. The most interesting feature of the crystal structure is the presence of channels running along the crystallographic *c* axis (Figure 1). The crystallization water molecules are hosted in these channels, with each one being hydrogen-bonded to one carboxylato oxygen atom (O4W···O2* = 2.786 Å, where * = −0.5 + *x*, *y*, 0.5 − *z*).

Textural characterization of **1** was carried out by measuring the adsorption−desorption isotherms of nitrogen at −196 °C. Figure S1 in the SI shows a typical Langmuir isotherm. The surface area was determined using the Langmuir protocol,[9] accordingly with the size of the pores of this material and with the composition of the pore walls (quasi homogeneous in polarity), both very close to those exposed by microporous zeolites. The surface area determined from this protocol is 610 m^2 g^{-1}. The pore size was determined using the Horwath−Kawazoe formalism,[10] which indicates a narrow pore-size distribution with a maximum of 7.94 Å. The pore volume determined from the same data amounts to 0.22 cm^3 g^{-1}.

The robustness of the crystals was checked by in situ powder X-ray diffraction (XRD) measurements at various temperatures (Figure 4a). The recorded diffractograms show that the structure of **1** is preserved up to 280 °C. After 280 °C (Figure 4b), a rapid collapse has been evidenced and the metal−organic framework (MOF) decomposed into CuO, a monoclinic phase (JCPDS 48-1548). Thermogravimetric−differential thermal analysis (TGA−DTA) experiments confirmed the powder XRD analysis. The TGA of **1** (Figure S2 in the SI) shows two mass losses: an endothermic one until around 140 °C and a second one, in the range 280−360 °C, accompanied by an exothermic effect. The first loss is assigned to the elimination of water, while the second loss corresponds to decomposition of the organic ligands.

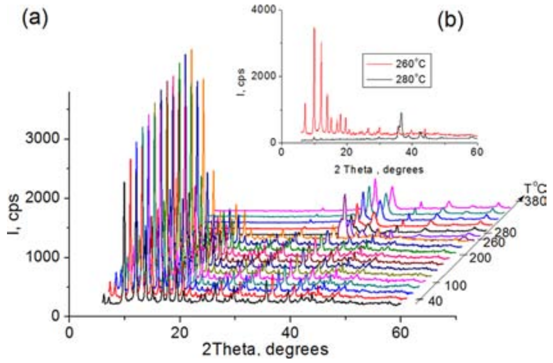

Figure 4. In situ measurement of the evolution of the XRD patterns with temperature (a) and XRD patterns after calcinations at 260 and 280 °C respectively (b).

In order to test the ability of **1** to host molecules other than water, several sorption experiments were carried out. For such a purpose, we considered molecules that exhibit current interest for storage, i.e., hydrogen (H_2) and carbon dioxide (CO_2).

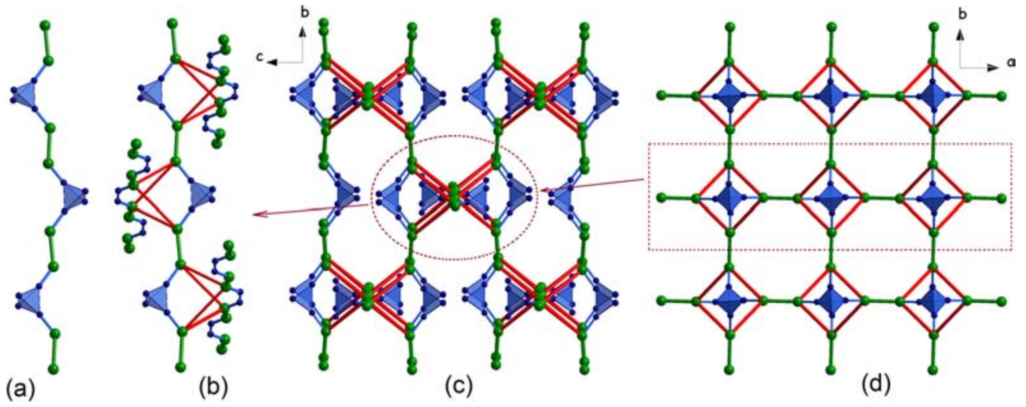

Figure 3. (a) Chains resulting from a connection of the binuclear nodes through hmt bridges. (b) {Cu_2(hmt)} chains connected by carboxylato bridges. (c) Simplified view along the crystallographic *a* axis. (d) Simplified view along the crystallographic *c* axis. The binuclear {$Cu_2(mand)_2$} nodes are represented as green rods; the hmt molecules are represented as blue tetrahedra; the carboxylato bridges are represented as red rods.

These experiments checked the capability of the new synthesized MOF to capture and store these molecules under ambient conditions.

Figure 5 shows the evolution of the adsorption uptakes for H_2 and CO_2. The H_2 and CO_2 molecules were adsorbed in volumes that correlate very well with the texture of this MOF, i.e., 10.9 cm^3 g^{-1} for H_2 (representing 0.09 wt %) and 90.7 cm^3 g^{-1} for CO_2 (representing 17.9 wt %). To obtain more information about this behavior, additional temperature-programmed desorption (TPD), TGA, and diffuse-reflectance infrared Fourier transform (DRIFT) experiments have been carried out for CO_2. All of these measurements showed that desorption occurs completely before 100 °C, while the degassed material was able to take up another volume of CO_2. CO_2-TPD experiments indicated (Figure S3 in the SI) desorption of CO_2 corresponding to 78.7 cm^3 g^{-1}. Figure S4 in the SI shows the comparative DRIFT and CO_2-DRIFT spectra of the investigated MOF. After adsorption, new bands corresponding to CO_2 were observed at 2337 and 2360 cm^{-1}, which are assigned to the asymmetric stretching vibration.[11] Degassing these samples by simple flushing of nitrogen at 50 °C led to the complete recovery of the spectrum of compound **1**.

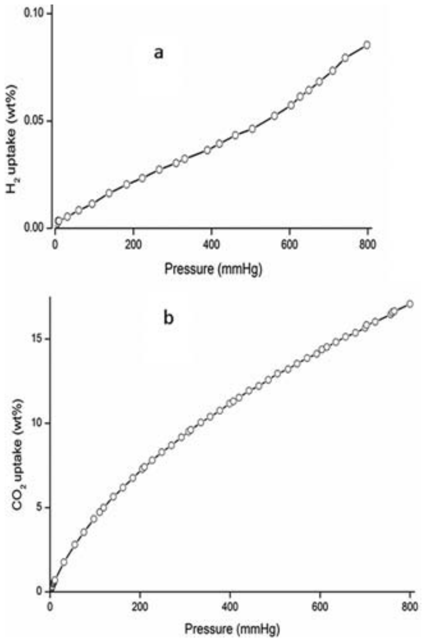

Figure 5. Adsorption uptakes of H_2 (a) and CO_2 (b) at room temperature.

Further studies of this and on similar compounds, focusing on their catalytic properties, are in progress in our laboratories.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, synthesis, crystallographic data, textural characterization of **1**, and experimental details on sorption studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) For example, see: (a) Férey, G.; Serre, C. *Chem. Soc. Rev.* **2009**, *38*, 1380. (b) Leong, W. L.; Vittal, J. J. *Chem. Rev.* **2011**, *111*, 688. (c) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695. (d) Lin, X.; Jia, J.; Hubberstay, P.; Schröder, M.; Champness, N. R. *CrystEngComm* **2007**, *9*, 438. (e) Janiak, C. *Dalton Trans.* **2003**, 2781. (f) Tranchemontagne, D. J.; Ni, Z.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5136. (g) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (h) Braga, D.; Grepioni, F. *Chem. Commun.* **2005**, 3635. (i) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (j) O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 675. (k) Stock, N.; Biswas, S. *Chem. Rev.* **2012**, *112*, 933.

(2) (a) Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450. (b) Czaja, A. U.; Trukhan, N.; Müller, U. *Chem. Soc. Rev.* **2009**, *38*, 1284.

(3) (a) Kahn, O. *Acc. Chem. Res.* **2000**, *33*, 647. (b) Andruh, M. *Chem. Commun.* **2011**, *47*, 3025. (c) Pardo, E.; Ruiz-Garcia, R.; Cano, J.; Ottenwaelder, X.; Lescouëzec, R.; Journaux, Y.; Lloret, F.; Julve, M. *Dalton Trans.* **2008**, 278. (d) Maspoch, D.; Ruiz-Molina, D.; Veciana, J. *Chem. Soc. Rev.* **2007**, *36*, 770. (e) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (f) Rogez, G.; Viart, N.; Drillon, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 1921. (g) Zheng, W.; Xiong, R.-G. *Chem. Rev.* **2012**, *112*, 1163.

(4) (a) McDonald, T. M.; D'Alessandro, D. M.; Krishna, R.; Long, J. R. *Chem. Sci.* **2011**, *2*, 2022. (b) Li, J.-R.; Ma, Y.; McCarthy, M. C.; Sculley, J.; Yu, J.; Jeong, H.-K.; Balbuena, P. B.; Zhou, H.-C. *Coord. Chem. Rev.* **2011**, *255*, 1791. (c) Montoro, C.; Linares, F.; Quartapelle Procopio, E.; Senkovska, I.; Kaskel, S.; Galli, S.; Masciocchi, N.; Barea, E.; Navarro, J. A. R. *J. Am. Chem. Soc.* **2011**, *133*, 11888. (d) Xie, S. M.; Zhang, Z. J.; Wang, Z. Y.; Yuan, L. M. *J. Am. Chem. Soc.* **2011**, *133*, 11892. (e) Morris, R. E.; Whealtley, P. S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4966. (f) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869. (g) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232.

(5) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1461.

(6) (a) Andruh, M. *Pure Appl. Chem.* **2005**, *77*, 1685. (b) Tudor, V.; Marin, G.; Kravtsov, V.; Simonov, Yu. A.; Lipkowski, J.; Brezeanu, M.; Andruh, M. *Inorg. Chim. Acta* **2003**, *353*, 35. (c) Paraschiv, C.; Andruh, M.; Ferlay, S.; Hosseini, M. W.; Kyritsakas, N.; Planeix, J.-M.; Stanica, N. *Dalton Trans.* **2005**, 1195. (d) Marin, G.; Tudor, V.; Kravtsov, V. Ch.; Schmidtmann, M.; Simonov, Yu. A.; Müller, A.; Andruh, M. *Cryst. Growth Des.* **2005**, *5*, 279. (e) Marin, G.; Andruh, M.; Madalan, A. M.; Blake, A. J.; Wilson, C.; Champness, N. R.; Schröder, M. *Cryst. Growth Des.* **2008**, *8*, 964.

(7) Hao, H.-Q.; Liu, W.-T.; Lin, Z.-J.; Tong, M.-L. *CrystEngComm* **2009**, *11*, 967.

(8) Kirillov, A. M. *Coord. Chem. Rev.* **2011**, *255*, 1603.

(9) Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1631.

(10) Horvath, G.; Kawazoe, K. J. *Chem. Eng. Jpn.* **1983**, *16*, 470.

(11) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724.