J|A|C|S
COMMUNICATIONS

Permeability of a Seemingly Nonporous Crystal Formed by a Discrete Metallocyclic Complex

Liliana Dobrzańska, Gareth O. Lloyd, Helgard G. Raubenheimer, and Leonard J. Barbour*

Department of Chemistry, University of Stellenbosch, Matieland 7602, South Africa

Received October 19, 2005; E-mail: ljb@sun.ac.za

Over the past decade the engineering of porosity in crystalline solids has become a highly active area of investigation.[1] The better-known systems implicated in these studies include zeolites, organic molecular crystals,[2] and metal−organic frameworks,[3] and one of the most important considerations addressed in these reports concerns the size of the pore openings. On the other hand, we[4] and others[5] have recently reported studies of materials that are highly permeable despite their seemingly nonporous solid-state structures (while interstitial lattice voids are present, the voids are not interlinked by channels). The few examples of such materials that are currently known to exist all consist of molecular organic crystalline materials composed of calixarenes[4] or similarly shaped molecules.[5] As part of our studies of discrete macrocyclic species that stack to form porous materials in the crystalline solid state,[6] we have synthesized a complex that forms lattice voids in the solid state but does not yield a conventionally porous arrangement. Furthermore, we show that sorption of small gas molecules by this material is possible despite the absence of pores in the static solid-state structure.

Slow evaporation of a methanolic solution of $CuCl_2\cdot 2H_2O$ and the exo-bidentate ligand 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene[7] (bitmb) in a 1:1 molar ratio afforded single crystals (**1**) suitable for X-ray diffraction analysis.[8] A discrete dinuclear metallocyclic complex $[Cu_2(bitmb)_2Cl_4]$ is formed as shown in Figure 1. Each copper ion is coordinated to two chloride anions and two bitmb ligands in a distorted square planar arrangement with like ligands trans to one another. The complex rings are canted at an angle of approximately 40° with respect to the crystallographic *a* axis, along which they are stacked one above the other to form linear columns. Both the shape and the columnar stacking arrangement of $[Cu_2(bitmb)_2Cl_4]$ are highly reminiscent of a silver complex recently reported by us[6] where the packing mode results in the formation of infinite one-dimensional solvent-filled channels that can readily be emptied of their contents to yield a porous material capable of absorbing a variety of gases. In the crystallographic model of the present structure, the space within the complex ring is occupied by a hydrogen-bonded ($O\cdots O = 2.769(8)$ Å) adduct consisting of one water molecule and one molecule of methanol.[9] The solvent adduct is disordered equally over two positions across a crystallographic inversion center, and the methanol oxygen atoms are weakly associated with the copper ions at a distance of 2.461(3) Å and situated at the apex of a pseudo square pyramid.

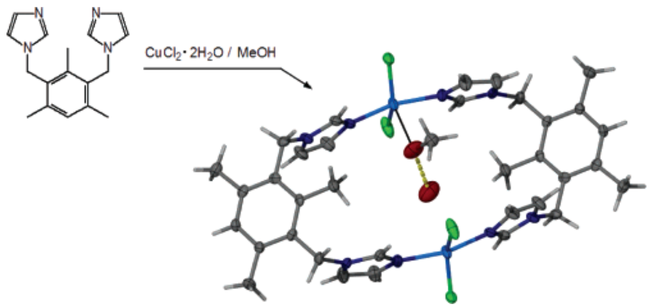

Figure 1. Formation of $[Cu_2(bitmb)_2Cl_4]\cdot CH_3OH\cdot H_2O$. Atoms are shown with 70% probability thermal ellipsoids. The $MeOH\cdots H_2O$ hydrogen bond is indicated as a fragmented yellow cylinder, and the Cu−MeOH contact is represented as a black line. The $MeOH\cdots H_2O$ adduct is disordered over two positions and only one of these instances is shown. Colors: carbon, gray; hydrogen, white; nitrogen, dark blue; oxygen, red; copper, light blue; chloride, green.

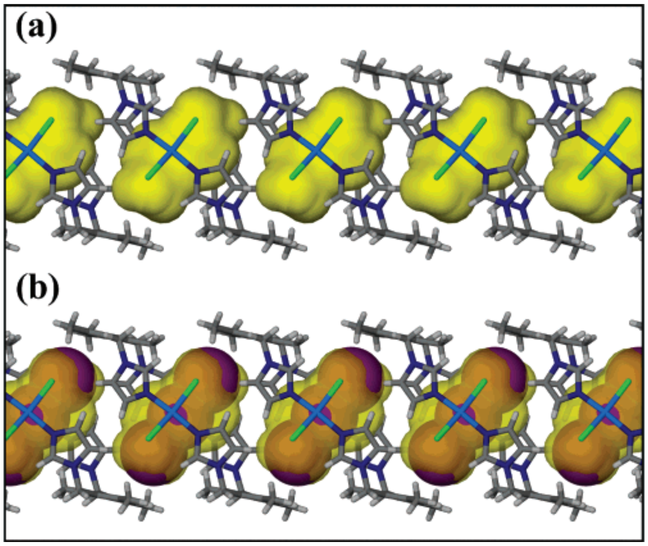

Figure 2. Columns of $[Cu_2(bitmb)_2Cl_4]$ with guest-accessible pockets shown as yellow Connolly surfaces ($r = 1.4$ Å, volume = ca. 108 Å^3): (a) the guest-free structure **2** and (b) the structure of **3** showing the disordered iodine molecules situated in the guest cavities. Protrusion of the iodine van der Waals surface beyond the Connolly surface implies the presence of weak intermolecular interactions in these regions.

Thermogravimetric analysis of the crystals reveals that solvent loss occurs readily, even at room temperature. Heating of the crystals at 60 °C under vacuum for 1 h results in complete removal of the solvent molecules, while the crystals (**2**) show no visible signs of mechanical stress. X-ray diffraction analysis[10] confirms that no significant change of the structure occurs on desolvation, except that the space previously occupied by solvent molecules becomes devoid of any appreciable electron density. It is interesting to note that, after desolvation, the crystals do not appear to absorb water even after exposure to the atmosphere for three weeks. A detailed Connolly[11] surface analysis (using a probe of radius $r = 1.4$ Å) reveals that, unlike the structure of our previously reported silver analogue,[6] the host lattice is not porous in the conventional sense. The solvent molecules of **1** are situated in discrete pockets as shown in Figure 2a, and a spherical probe with $r < 1.33$ Å is required in order to map a continuous channel (i.e. for the structure determined at 100 K). After solvent removal, a channel can only be mapped using $r < 0.89$ Å at 100 K and $r < 0.96$ Å at 293 K.

10.1021/ja057122h CCC: $33.50

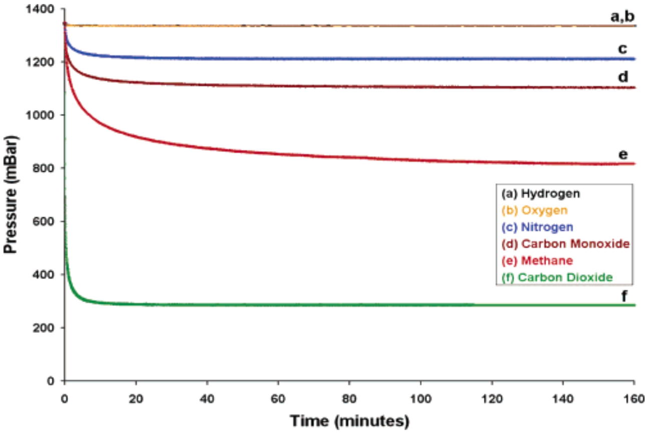

Figure 3. Gas sorption isotherms for H_2, O_2, N_2, CO, CH_4, and CO_2 (using a 1.101 g sample of **2** placed in a chamber of volume 8.53 cm^3). The sample chamber was evacuated between experiments in order to remove any residual gas. Note that the isotherms for H_2 and O_2 are indistinguishable from one another.

Solvent loss without collapse of the packing arrangement of the host complexes implies that the crystals are permeable to small molecular entities despite their seemingly nonporous structure. We therefore exposed a sample of **2** to a variety of gases (Figure 3) in order to investigate its ability to behave as a conventionally porous functional material. Sorption isotherms were recorded volumetrically[4a] at room temperature for H_2, O_2, N_2, CO, CH_4, and CO_2, each with an initial pressure of approximately 1.35 atm. Figure 3 shows that **2** is indeed permeable to gases and, furthermore, that there is significant selectivity between the different gases tested. At relatively low pressures of <1.35 atm, carbon dioxide is absorbed most readily, followed by methane, carbon monoxide, and nitrogen. Oxygen and hydrogen are only absorbed in very small quantities.

To further probe the permeability of **2**, a single crystal was exposed to iodine vapor in a sealed vial for 25 h. After exposure, the color of the crystal changed from green to brown with no discernible degradation of its macroscopic integrity. X-ray analysis[12] of the new phase (**3**) reveals the presence of iodine in the guest pockets as shown in Figure 2b. Each iodine molecule is disordered equally over two positions with a total site occupancy of 1 within each pocket. In the disordered model, one of the iodine atoms is situated on a crystallographic inversion center and at a distance of 3.458(1) Å from each copper ion. Although too long to be considered a coordination bond, this distance, and thus the consistent location of an iodine atom at this site, is likely due to a weak Cu···I electrostatic interaction. The I−I bond length is 2.648(1) Å and is in the slightly low to normal range. The arrangement of the host complexes in **3** is essentially identical to that in **1** and **2**. In **3** a probe with $r < 1.24$ Å is required in order to map an open channel (note that the van der Waals radius of iodine is generally taken to be approximately 1.98 Å[13]).

In conclusion, we have described the static crystal structural variants of a highly permeable metal−organic material that does not possess conventional pores. That the crystals absorb a variety of gases, including molecules as large as iodine, is non-intuitive from a simple assessment of the solid-state structures. Previously this phenomenon had only been observed for a small number of materials consisting of calixarenes[4] or similarly shaped cup-like organic molecules[5] packed in bilayers. Our results show that the concept of porosity in seemingly nonporous crystals is general and not confined only to specific types of molecules or structures. On the basis of the observation that the macroscopic integrity of the single crystal is preserved during the guest uptake and release processes, it has been suggested[4d] that the host molecules might cooperate with one another in a dynamic and concerted fashion in order to create windows of opportunity, thus allowing mobile guest molecules to freely traverse the crystals.

Acknowledgment. The authors thank the National Research Foundation of South Africa and the Claude Harris Leon Foundation for support of this work. L.D. also thanks Nicolaus Copernicus University for study leave.

Supporting Information Available: Crystallographic data (CIF) for **1**−**3** as well as thermogravimetric analysis of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Rowsell, J. L.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670. (b) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109. (c) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305. (d) Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.

(2) (a) Malek, N.; Maris, T.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **2005**, *127*, 5910. (b) Ooms, K. J.; Campbell, K.; Tykwinski, R. R.; Wasylishen, R. E. *J. Mater. Chem.* **2005**, *15*, 4318.

(3) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276. (c) Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem., Int. Ed.* **2003**, *43*, 2334.

(4) (a) Atwood, J. L.; Barbour, L. J.; Thallapally, P. K.; Wirsig, T. B. *Chem. Commun.* **2005**, *1*, 51. (b) Thallapally, P. K.; Wirsig, T. B.; Atwood, J. L.; Barbour, L. J. *Chem. Commun.* **2005**, *35*, 4420. (c) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 2948. (d) Atwood, J. L.; Barbour, L. J.; Jerga, A.; Schottel, B. L. *Science* **2002**, *298*, 1000.

(5) Riddle, J. A.; Bollinger, J. C.; Lee, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 6689.

(6) Dobrzańska, L.; Lloyd, G. O.; Raubenheimer, H. G.; Barbour L. J. *J. Am. Chem. Soc.* **2005**, *127*, 13134.

(7) Liu, H.-K.; Hu, J.; Wang, T.-W.; Yu, X.-L.; Liu, J.; Kang, B. *Dalton Trans.* **2001**, *23*, 3534.

(8) Crystal data for **1**: $C_{35}H_{43}Cl_4Cu_2N_8O_2$, $M = 876.65$, green prism, $0.20 \times 0.10 \times 0.10$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.4349(11)$ Å, $b = 10.7308(14)$ Å, $c = 22.018(3)$ Å, $\beta = 99.379(2)°$, $V = 1966.2(4)$ Å^3, $Z = 2$, $D_c = 1.481$ g/cm^3, $F_{000} = 902$, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.5°$, 11 696 reflections collected, 4549 unique ($R_{int} = 0.0399$). Final GOF = 1.059, $R_1 = 0.0574$, $wR_2 = 0.1359$, R indices based on 3638 reflections with $I > 2\sigma(I)$ (refinement on F^2), 234 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.396$ mm^{-1}.

(9) The electron density within the solvent pocket is consistent with a model comprising a hydrogen-bonded MeOH···H_2O adduct disordered over two positions. This model is supported by an apparent intermolecular O···O distance between methanol and water of 2.769(8) Å, which is consistent with hydrogen bonding. Since solvent loss occurs at room temperature, it is not feasible to use thermogravimetric analysis to reliably determine the solvent content of **1**. We therefore concede the possibility that our solvent model may be incorrect but add that this does not affect the main finding of our study.

(10) Crystal data for **2**: $C_{34}H_{40}Cl_4Cu_2N_8$, $M = 829.62$, green prism, $0.20 \times 0.10 \times 0.10$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.362(6)$ Å, $b = 10.550(8)$ Å, $c = 22.438(16)$ Å, $\beta = 99.093(14)°$, $V = 1954(3)$ Å^3, $Z = 2$, $D_c = 1.410$ g/cm^3, $F_{000} = 852$, MoKα radiation, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $2\theta_{max} = 57.2°$, 11 765 reflections collected, 4587 unique ($R_{int} = 0.1231$). Final GOF = 0.789, $R_1 = 0.0640$, $wR_2 = 0.1180$, R indices based on 1850 reflections with $I > 2\sigma(I)$ (refinement on F^2), 217 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.396$ mm^{-1}. This structural analysis was performed at room temperature in order to obtain accurate parameters for the material at the same temperature at which gas sorption experiments were conducted.

(11) Connolly, M. L. *Science* **1983**, *221*, 709.

(12) Crystal data for **3**: $C_{34}H_{40}Cl_4Cu_2I_2N_8$, $M = 1083.42$, brown prism, $0.20 \times 0.15 \times 0.10$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.3975(18)$ Å, $b = 10.861(2)$ Å, $c = 21.890(5)$ Å, $\beta = 98.340(4)°$, $V = 1975.5(7)$ Å^3, $Z = 2$, $D_c = 1.821$ g/cm^3, $F_{000} = 1064$, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.5°$, 12 192 reflections collected, 4593 unique ($R_{int} = 0.0721$). Final GOF = 1.026, $R_1 = 0.0670$, $wR_2 = 0.1360$, R indices based on 2998 reflections with $I > 2\sigma(I)$ (refinement on F^2), 235 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 2.947$ mm^{-1}.

(13) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

JA057122H