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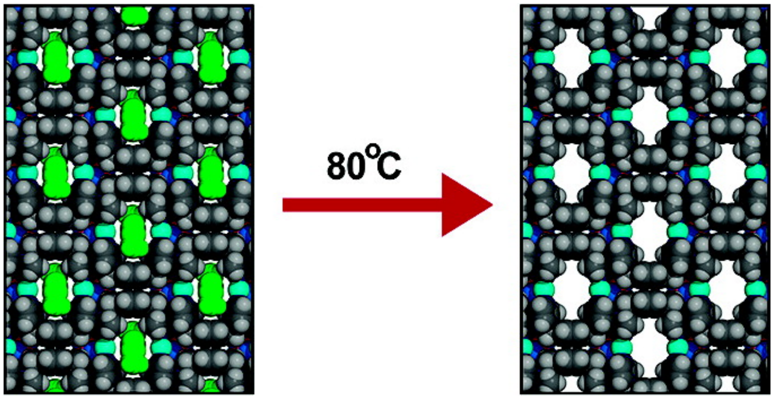

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A Discrete Metallocyclic Complex that Retains Its Solvent-Templated Channel Structure on Guest Removal to Yield a Porous, Gas Sorbing Material

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The sorption of gases has recently been thrust into the limelight as a direct result of current pressing demands for viable gas storage and separation technologies, especially with regard to the so-called "Hydrogen Economy".[1] Through the pioneering work mainly of Yaghi and Kitagawa, metal organic frameworks (MOFs) have become the focus of many research efforts worldwide.[2] Although some success has been achieved using these types of coordination polymeric materials, the ultimate goals of 6 and 35% by weight (wt %) for hydrogen and methane storage, respectively, are still far from realization.[3] The most widely applied method of producing porous crystals is to assemble a coordination polymeric MOF with solvent molecules trapped in its lattice and, subsequently, to extricate the solvent without disrupting the host framework. The utilization of robust *exo*-bidentate metal−ligand−metal bridges is crucial for the success of this approach because weakly coordinating complexes generally rearrange upon desolvation to form a different, yet also efficiently packed phase.[4] Indeed, with only a few known exceptions,[5] rearrangement to achieve close-packing upon solvent removal is almost always observed for organic molecular crystals,[6] as well as for metal−organic complexes.[7] Here, we report the formation of a crystalline solvate by a discrete cyclic dinuclear silver complex. The rectangular host complexes are stacked to form channels that entrap acetonitrile guest molecules. Upon removal of the guest, the packing arrangement of the host is preserved, thus yielding a porous lattice capable of absorbing various gases.

Slow evaporation of an equimolar solution of $AgBF_4$ and the ditopic ligand 1,4-bis(2-methylimidazol-1-ylmethyl)benzene[8] (L) in acetonitrile (Figure 1) yielded single crystals (**1**) suitable for X-ray diffraction analysis.[9] The crystallographic study reveals a discrete rectangular complex composed of two linearly coordinated silver ions doubly bridged to one another by means of two ligands (Figure 1). The ring-like complexes are stacked along the crystallographic *c* axis to form one-dimensional channels, as shown in Figure 2. Acetonitrile solvent molecules occupy the channels, while the BF_4 anions are situated between adjacent columns of stacked $[Ag_2L_2]^{2+}$ complexes. Each column is in van der Waals contact with six neighboring columns (Figure 3) to form a "brick wall" packing motif as viewed along [001]. This arrangement is stabilized by intermolecular offset $\pi\cdots\pi$ interactions between imidazole rings along [010] (interplanar spacing = 3.44 Å) and benzene rings along [100] (interplanar spacing = 3.52 Å).

Thermogravimetric analysis of **1** shows that the acetonitrile guest molecules can be removed completely by heating the crystals to >80 °C. Using hot stage microscopy, crystals heated to 80 °C were observed to remain intact and transparent. A crystal thus treated (**2**) was therefore subjected to single-crystal X-ray analysis,[10] which showed that no rearrangement of the host lattice takes place as a result of thermally induced desolvation. No electron density peaks were located within the channels previously occupied by the acetonitrile guests.

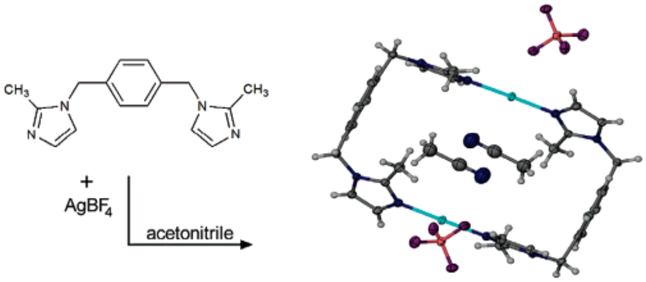

Figure 1. Formation of $[Ag_2L_2](BF_4)_2{\cdot}2CH_3CN$, where L = 1,4-bis(2-methylimidazol-1-ylmethyl)benzene.

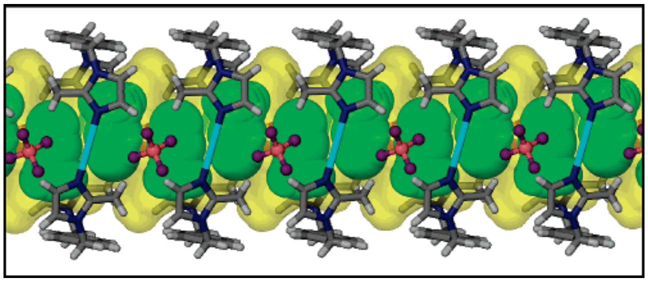

Figure 2. Perspective view perpendicular to a one-dimensional channel (semitransparent yellow surface) defined by a column of cyclic $[Ag_2L_2]^{2+}$ complexes. The complex ions $[Ag_2L_2]^{2+}$ are shown as capped-sticks, the BF_4^- ions as balls-and-sticks, and the acetonitrile molecules are shown in the van der Waals metaphor. Colors: carbon, gray; hydrogen, white; nitrogen, dark blue; silver, light blue; boron, pink; fluorine, purple; acetonitrile, green.

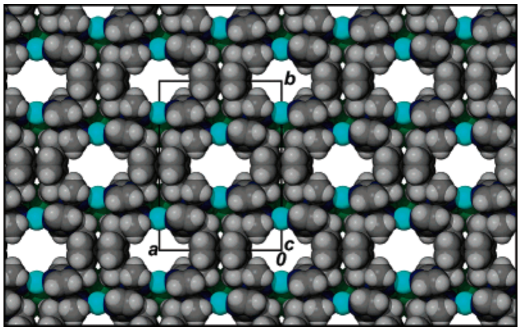

Figure 3. Space filling projection showing the packing arrangement of rectangular $[Ag_2L_2]^{2+}$ host complexes to form channels along [001]. Colors: carbon, gray; hydrogen, white; nitrogen, dark blue; silver, light blue.

The vacant channels of **2** are approximately rectangular in cross-section with internal van der Waals dimensions of ca. 4.9 × 7.5 Å. The unoccupied space in the crystal is estimated to be approximately 22% of the total volume.[11] Although this value is lower than that calculated for many of the vacant MOFs reported to date, it has been suggested that smaller pore dimensions are desirable in order

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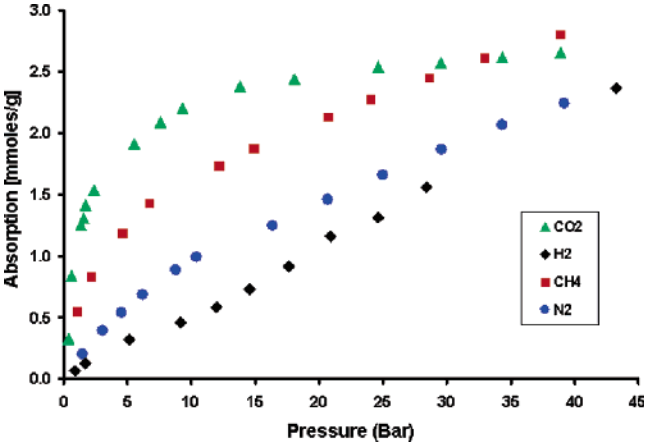

Figure 4. Gas sorption isotherms for phase **2** recorded at 30 °C.

to increase van der Waals contact area and hence to improve gas binding affinity.[12] It has also been suggested that exposed faces of aromatic groups and "naked" metal centers might present favorable sorption sites for hydrogen gas.[13]

Crystals of **1** were heated at 80 °C under vacuum for 3 h in order to effect conversion to phase **2**. The sample was crushed, and gas sorption isotherms were recorded (see Figure 4) for CO_2, N_2, CH_4, and H_2 at 30 °C using a previously described device.[14] At low pressure (<10 bar) the bulky gases are absorbed more readily, presumably as a result of their more favorable binding affinities with the pore surface. However, at higher pressures (>48 bar), the smaller gases are absorbed in larger molar quantities, as might be expected based on space filling criteria. To date, most studies of H_2 sorption by MOFs have been conducted at 77 K, while relatively few reports of room temperature experiments have been published.[12b,c] The hydrogen sorption capacity of phase **2** (i.e., ca. 1 wt % at 78 bar and 30 °C) compares favorably with these previously reported results.

In summary, we have described a discrete rectangular metal−organic complex that stacks to form one-dimensional channels filled with acetonitrile solvent molecules. Removal of the solvent under relatively mild conditions proceeds via a single-crystal to single-crystal transformation that leaves the host lattice unaltered. Our findings proffer a design strategy for porous materials based on the simple principle that rigid molecular rings cannot pack efficiently and would thus favor the inclusion of guest species whenever possible. Upon guest removal, an efficiently packed new phase can then only be achieved by means of bond cleavage. Thus, achieving crystal porosity by maintaining robust metal−ligand coordination bonds in such discrete cyclic systems directly parallels the strategy employed for MOFs.

We note that an approach based on the use of flexible metallacyclic ensembles has been outlined, but that in such cases the guest-free structures are poorly characterized.[15] Consequently, although these transformed materials have exhibited gas sorption ability, their crystal structures are not known. The formation of porous materials by means of single-crystal transformations[16] is of significant value because this allows one to study the structural features of a gas sorption substrate at the atomic scale in the hope of ultimately understanding the underlying principles that govern gas−solid interactions.

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Supporting Information Available: Crystallographic data (CIF files) for **1** and **2**, thermogravimetric analysis for **1**, and gas sorption plot of wt % versus pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for $C_{36}H_{42}Ag_2B_2F_8N_{10}$: $M = 1004.16$, $0.25 \times 0.20 \times 0.15$ mm^3, monoclinic, space group $C2/m$ (No. 12), $a = 14.911$ (1), $b = 20.138$ (1), $c = 7.0209(5)$ Å, $\beta = 90.293$ (1)°, $V = 2108.2(3)$ Å^3, $Z = 2$, $D_c = 1.582$ g/cm^3, $F_{000} = 1008$, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.4°$, 6675 reflections collected, 2520 unique ($R_{int} = 0.0203$). Final GOF = 1.062, $R1 = 0.0257$, $wR2 = 0.0625$, R indices based on 2413 reflections with $I > 2\sigma(I)$ (refinement on F^2), 139 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.004$ mm^{-1}.

(10) Crystal data for $C_{32}H_{36}Ag_2B_2F_8N_8$: $M = 922.05$, $0.25 \times 0.20 \times 0.10$ mm^3, monoclinic, space group $C2/m$ (No. 12), $a = 14.831(1)$, $b = 20.564$ (1), $c = 7.0449(5)$ Å, $\beta = 90.118$ (1)°, $V = 2148.5(3)$ Å^3, $Z = 2$, $D_c = 1.425$ g/cm^3, $F_{000} = 920$, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.5°$, 6760 reflections collected, 2555 unique ($R_{int} = 0.0199$). Final GOF = 1.071, $R1 = 0.0267$, $wR2 = 0.0639$, R indices based on 2430 reflections with $I > 2\sigma(I)$ (refinement on F^2), 120 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.977$ mm^{-1}.

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