Metal-promoted assembly of organic-based cages into a porous material

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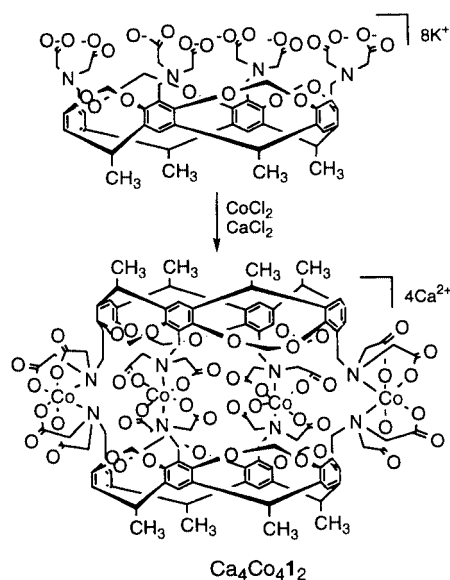
Metal-assembled cages form grids in the solid-state and pack into a manner that creates a material with pores and channels.

Zeolites are very valuable because of their extensive use as molecular sieves, catalysts, and ion exchange materials.[1] One essential feature to zeolites is their porous structure. We have synthesized a porous material, $Ca_4Co_4\mathbf{1}_2 \cdot xH_2O$, composed of metal and organic components that has a zeolite like porous structure and adsorbs water. This material is a part of an expanding area of metal–organic frameworks which have porous structures, but are not based on silicates or aluminates.[2] These new materials are important because they have different properties than those of zeolites, and may be used as specific catalysts for organic transformations or selective trapping agents. Even though part of their framework is organic, these materials retain their structure after water or solvent molecules are removed and up to temperatures of 300 °C.[2]

Similar to porous metal–organic materials are the metal-assembled supramolecular compounds that form squares, arrays, grids, ladders, sheets and even cages.[3] The assembly of nonporous metal compounds, like the formation of porous metal–organic frameworks, relies on the coordination ability of metal ions and the proper choice of organic ligand. Both of these classes of compounds may have infinite structures, however, the porous materials have often been investigated for adsorptivity. The non-porous metal-assembled compounds sometimes have cavities that encapsulate guests or solvent molecules.[4] The metal-assembled cages act as molecular boxes that bind guests until the cages are signaled by pH change to open and allow guest release.

During our research on metal-assembled cage molecules (Scheme 1), we have discovered that the cages assemble into arrays linked by coordinating cations. The array formation is promoted by the presence of carboxylate groups on four sides of the cages, which are positioned 90° apart in a nearly planar arrangement. Carboxylate groups, having two oxygens and more than one lone pair of electrons on each oxygen, can bind to more than one metal ion and in some cases help create porous materials. Examples of bridging carboxylate groups are very common in metalloproteins and small molecule models of metalloproteins, where metal centers are linked by carboxylates from amino acids or alkyl carboxylates.[5] The four carboxylate groups in $Ca_4Co_4\mathbf{1}_2 \cdot xH_2O$ come from **1**, which is a cup-shaped resorcinarene molecule that has four pairs of carboxylates positioned on its upper rim. These carboxylates coordinate to transition metal ions and, in the process, form octaanionic cage complexes.[6] One can think of the carboxylate groups on the cages as four metal binding sites equally spaced from each other around the middle of an ellipsoid.

Owing to the anionic nature of these metal-assembled cages, counter cations are associated with them. When calcium is the counter cation and an aqueous solution of cobalt-assembled cages is allowed to crystallize by slow diffusion of isopropyl alcohol, the calcium ions coordinate to oxygen atoms of the carboxylates and in so doing form $Ca_4Co_4\mathbf{1}_2 \cdot xH_2O$.† This bonding of oxophilic calcium ions to carboxylate oxygens is not unusual, but what is novel is that the calcium ions coordinate to carboxylates from two cages and create a bridge between two cages. In addition to coordinating to carboxylate oxygens, the calcium ions also coordinate to water molecules, which complete their coordination sphere. As the calcium ions bring together two cages, they assemble a two-dimensional array of cages (Fig. 1).‡ The cages are *ca.* 18 Å apart from each other (center of one cage to the center of the next nearest cage). When the rows of cages line up, voids are formed which would have diameters of *ca.* 15 Å, except that they contain water molecules that are a part of a ring of molecules hydrogen-bonded together around the cages. Thus, the voids have edge lengths of *ca.* 9.5 Å (Ca to Ca van der Waals radii).

The placement of the next layer of cages is also of interest. Though the voids of one layer would seem to be the optimum place for the cages of the next layer, the cages do not position themselves there, but rather lie over the cation bridges of the first layer.[7] In so doing, rhombic pores and channels form

Scheme 1
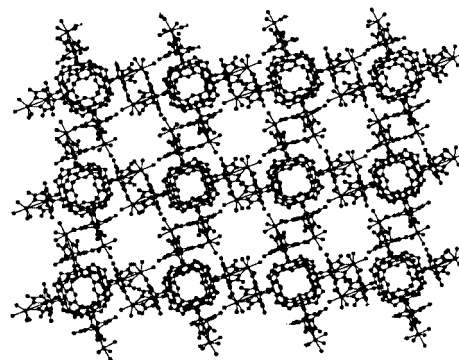
Fig. 1 A top view of $Ca_4Co_4\mathbf{1}_2$ from the X-ray crystal structure showing the packing of the cages into two-dimensional arrays with linking calcium ions. Note the four carboxylate groups are on the exterior of the cages, 90° apart, and help connect the cages together.
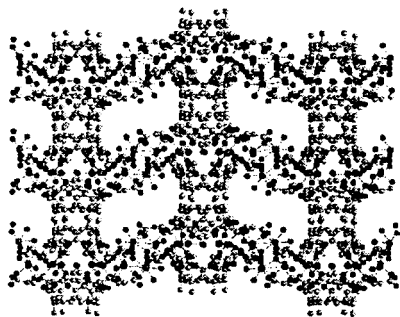
Fig. 2 A side view of $Ca_4Co_4\mathbf{1}_2$ showing the packing of three layers of cages and the channels connecting the pores. The cages in the middle layer are behind the first and third layers. The first and third layers are separated by carboxylate groups of the middle layer. The water molecules within the channels have been omitted for clarity.

(Fig. 2). Cages line two sides of the pores while carboxylates and calcium ions occupy the other four sides. Owing to the presence of both phenyl, methyl, and carboxylate groups on the cages, the pores have both a nonpolar and polar nature. Since the carboxylates do not fill the whole side of a pore as the cages do, channels lead into the pores from two directions. The pores are roughly shaped like hexagons, $9.5 \times 9.5 \times 21$ Å, with two of the long sides occupied by cages. The connecting channels have 5×12 Å edges and since they are lined with carboxylate oxygens and water molecules bound to calcium ions, they are expected to be hydrophilic and variable in size depending on the amount of water bound to calcium. Fig. 2 shows that a line of cages is linear in one direction and zigzaged in the other. This is because the bridging carboxylate arms of the cages are side-by-side or one on top of the other.

An important property of porous materials is their ability to retain molecules within their pores. The pores of Ca_4-$Co_4\mathbf{1}_2 \cdot x\mathrm{H}_2\mathrm{O}$ are occupied by water and isopropyl alcohol molecules. Some water molecules are bound to the counter cations, some hydrogen bonded around the cages, and others disordered within the pores. This is similar to zeolites, where water is bound to cations within a silica or alumina framework. In an attempt to understand the material's affinity for water, we used thermogravametric analysis to measure the change in mass of the material as a function of temperature. When the temperature of the material is raised at a rate of $1\,°\mathrm{C\,min}^{-1}$ from 25 to 250 °C, initially, a fast rate of weight loss is observed up to 120 °C, after which weight is lost more slowly until the weight of the material becomes constant. The total weight loss accounts for 20% of the material and gives a 40:1 water to $Ca_4Co_4\mathbf{1}_2$ ratio. A composition of 20% water ranks this material with zeolites in water content.[1] The water to complex ratio of 40:1 is in good agreement with the ratio found by X-ray crystallography: 43:1.

Not surprisingly, after releasing water, this material adsorbs water. When the dehydrated material is cooled in the presence of a stream of water vapor (20 mm Hg), an initial fast rate of water uptake is observed below 90 °C, which leads into a slower rate of water adsorption as the temperature reaches ambient. The amount of water that was lost is regained. This process of dehydration and adsorption can be repeated without a significant change to the amount of water adsorbed. This is an indication that the material's internal structure remains intact and that heating and water removal do not cause decomposition. Another indication of retention of structural integrity is that the external block-shape of the crystals does not change during adsorption and dehydration. Further studies on the retention of structure are under way.

In conclusion, $Ca_4Co_4\mathbf{1}_2 \cdot x\mathrm{H}_2\mathrm{O}$ is a new metal–organic porous material composed of elaborate organic cage molecules and cations. Four perpendicular carboxylate-binding groups on the cage part of $Co_4\mathbf{1}_2^{8-}$ provide sites for calcium binding and the assembly of the cages into arrays. The packing of the layers of cages over the bridges of other layers creates pores and channels within the material. Metal-assembled cages and water molecules line the channels that link the pores. These pores and channels contain water, which can be removed and adsorbed. Future research will focus on the use of $C_4CO_4\mathbf{1}_2$ as a small molecule trapping agent, and the affect on pore size by the substitution of the calcium ions by other metal ions.

Notes and references

† *Synthesis* of $Ca_4Co_4\mathbf{1}_2 \cdot x\mathrm{H}_2\mathrm{O}$: this is performed in a similar manner to the synthesis of $Ba_4Co_4\mathbf{1}_2$, see ref. 6. To a solution of $Ba_4\mathbf{1} \cdot 24\mathrm{H}_2\mathrm{O}$ (33 mg, 0.016 mmol) dissolved in 1 M hydrochloric acid (1 mL) and water (2 mL) was added K_2SO_4 (17 mg). The white precipitate of $BaSO_4$ that formed was removed by filtration. Cobalt(II) chloride hexahydrate (9.0 mg, 0.038 mmol) and $CaCl_2$ were added to the solution and the pH raised to 5 by addition of K_2CO_3. Isopropyl alcohol was then layered over the solution. After two days, pink prismatic crystals of $Ca_4Co_4\mathbf{1}_2$ formed (18 mg, 36% yield). Anal. Calc. for $C_{112}H_{104}N_8O_{48}Ca_4Co_4 \cdot 24\mathrm{H}_2\mathrm{O}$: C, 42.58; H, 4.82; N, 3.55. Found: C, 42.83; H, 4.57; N, 3.31%.

‡ *Crystallographic data* for $Ca_4Co_4\mathbf{1}_2 \cdot 2(\mathrm{CH}_3)_2\mathrm{CHOH} \cdot 43\mathrm{H}_2\mathrm{O}$: $M = 3618$, pink color, dimensions $0.5 \times 0.4 \times 0.25$ mm, monoclinic, space group $C2/c$ (no. 15), $Z = 4$, $a = 18.598(4)$, $b = 27.575(8)$, $c = 37.106(8)$ Å, $\beta = 92.318(10)°$, $V = 19\,014(8)$ Å^3, $D_c = 1.199$ g cm^{-3}, $T = 292(2)$ K; Mo-Kα radiation ($\lambda = 0.71073$ Å); 9469 total data, 6209 $[F > 4\sigma(F)]$ observed independent reflections with $2.1 < \theta < 21°$ collected: $R = 0.0890$, $R_w = 0.1352$, GOF = 1.055. Crystals were mounted in a sealed capillary and immersed in mother liquor during analysis. Disordered water molecules were located in the crystal.

CCDC 182/1690. See http://www.rsc.org/suppdata/cc/b0/b003187i/ for crystallographic files in .cif format.

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