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SMTP-1: The First Functionalized Metalloporphyrin Molecular Sieves with Large Channels**

Kuan-Jiuh Lin*

In memory of Ta-shue Chou

Zeolites have emerged as an exciting area of supramolecular chemistry. In particular, crystalline zeolites or zeotypes with uniform pore sizes of 10 – 20 Å have diverse applications as catalysts, molecular sieves, and biosensors.[1–3] Recently, attention has turned toward organic and coordination zeolites to perform specific functions that are not available with inorganic zeolites. However, only a few examples of network structures with large cavities or channels have been demonstrated.[4] Moreover, the problems of fragility, acidity, and thermal stability of the host lattice have not been overcome.[5] Hence, the design and preparation of robust, air-stable, porous coordination zeolites provides a considerable challenge in materials chemistry.

We are exploring ways to construct new classes of coordination zeolites by hydrothermal synthesis,[6] a powerful technique often applied to the synthesis of zeolites. Encouraged by our recent success in exploiting the symmetry and functionality of the dianionic squarate ligand $C_4O_4^{2-}$ as a robust and rigid tether for the construction under hydrothermal conditions of coordination solids having open frameworks, we turned to the dianion tpyp (H_2tpyp = 5,10,15,20-tetrakis(4-pyridyl)porphyrin) as the molecular building block, as it has four equally spaced pyridyl groups linked to a porphyrin ring that gives it a rigid conformation. We surmised that the reaction of tpyp with a divalent first-row transition metal should yield a metalloporphyrinate material with nanometer-scale voids.[4c, 7] Porphyrin-based architectures have diverse potential applications as biomimetic models and as functional materials for the transport of energy, charge, molecules, and ions.[8]

We synthesized one cobalt(II) and two manganese(II) porphyrinates, which we collectively named SMTP-1 (*s*upramolecular *m*aterials in *T*aiwan *p*orphyrin, number 1), by employing hydro(solvent)thermal conditions. Crystals of all products were grown in a static autoclave at 200 °C under autogenous pressure for 48 h. Most reactions yielded bunched aggregates of individual crystals, but single crystals large enough for X-ray diffraction studies were also obtained.[9] Crystalline SMTP-1 is stable in air and is insoluble in water.

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The products were identified as neutral porous networks with the general formula $[\{M(tpyp)\}_6]\cdot G$ (**1**: $M = Co^{II}$, $G = 12\,CH_3COOH\cdot 12\,H_2O$; **2**: $M = Mn^{II}$, $G = 60\,H_2O$; **3**: $M = Mn^{II}$, $G = 12\,C_2H_5OH\cdot 24\,H_2O$) by single-crystal X-ray structure analysis, elemental analysis, thermogravimetric analysis, and FT-IR spectroscopy.

The structure of SMTP-1 consists of a layered framework with large cavities (Figure 1). In each layer, the secondary building blocks consist of the cyclic metalloporphyrin hexamer and spiropentamer.[10] Each metal center has local symmetry of $\bar{1}$ and is coordinated octahedrally by four nitrogen atoms of the porphyrin (average bond lengths: Co–N 1.994(5) Å for **1**; Mn–N 1.992(4) and 2.097(3) Å for **2** and **3**, respectively) and two nitrogen atoms of the *trans* pyridyl groups of tpyp (Co–N 2.292(5) Å for **1**; Mn–N 2.294(5) and 2.411(3) Å for **2** and **3**, respectively). The tpyp building block is engaged in a *trans*-$\mu_{1,3}$ coordination mode. As is common in 5,10,15,20-tetraarylporphyrins, large dihedral angles between the planes of the pyridine rings and the porphyrin are observed (110° for pyridine rings attached to metal centers, and 68° for the others). The compound SMTP-1 crystallizes in the rhombohedral space group $R\bar{3}$ and therefore lies around a crystallographic $\bar{3}$ position. This represents the maximum D_{3d} point group symmetry that can be attained by a $[\{M(tpyp)\}_6]$ species. Notable features of the SMTP-1 structure are the hexameric cage, which has an extra-large cavity with an interior diameter of 20 Å, and the functional pyridine windows (Figure 2). Furthermore, owing to the natural tendency of π overlap in porphyrin molecules, adjacent layers are "glued" by noncovalent π–π interactions, so that the cavities eclipse one another. This results in an infinite hexagonal channel along the crystallographic *c* axis (Figure 1). As anticipated, the hexagonal channels have the dimensions of $a/2 \times a/\sqrt{3}$ (17×20 Å). The effective pore size of 13×16 Å[11] is comparable to that of the mineral phosphate cacoxenite.[12] Although the pendant pyridyl groups protrude into the window, this metalloporphyrinate has an extremely

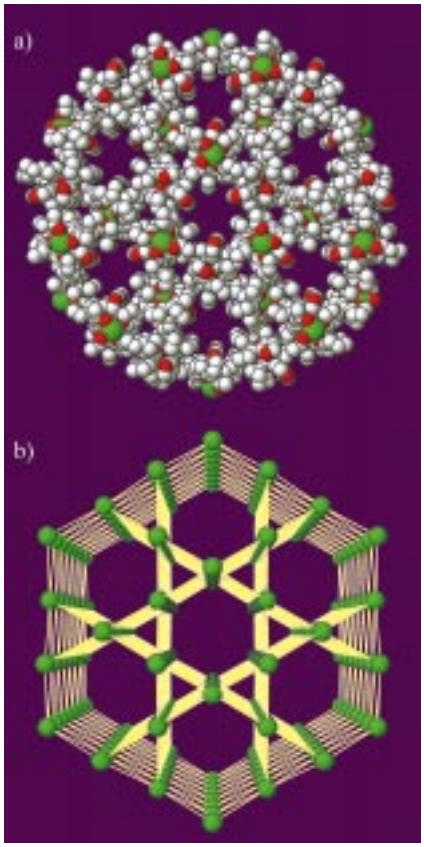

Figure 1. Perspective view of the open-framework structure of SMTP-1 along the crystallographic *c* axis. a) Space-filling representation. b) Skeletal representation (M···M connections). The hexagonal channels have the dimensions of $a/2 \times a/\sqrt{3}$ (17×20 Å). Hydrogen atoms and solvent molecules are omitted for clarity.

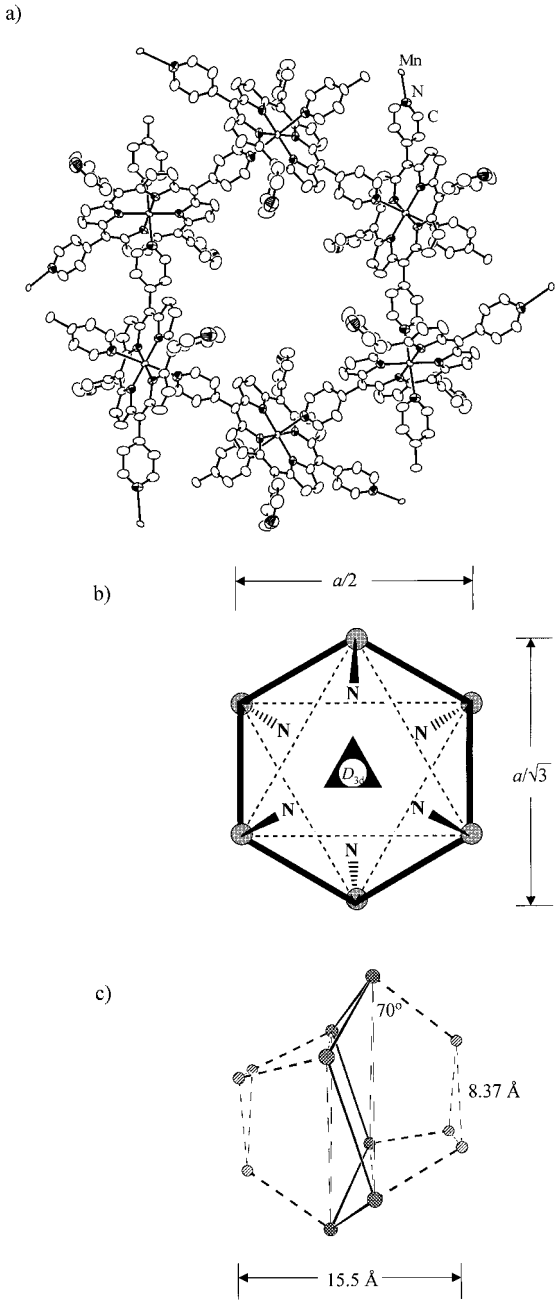

Figure 2. The hexameric cage has a polar cavity 17×20 Å across and 15 Å deep. a) ORTEP plot along the threefold *c* axis (50% probability ellipsoids). b) Skeletal representation in D_{3d} point group symmetry. c) View perpendicular to the C_3 axis. Cross-hatched: $M = Co^{II}$ or Mn^{II}; Shaded: N.

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open structure due to the long N···N distance (8.37 Å) between the pyridyl groups and the high projection angle (70°) (Figure 2c).

The most intriguing feature of the SMTP-1 structure is the presence of the highly disordered solvent molecules trapped in the pores or channels. The pore solvent molecules could not be completely located in the structure analysis and are not discussed here. Further studies by other methods are required to characterize them. Thermogravimetric analysis reveals that the guest molecules are liberated below 200 °C; however, the crystal lattice is thermally stable up to 400 °C.[13] Moreover, powder X-ray diffraction patterns showed that the porous framework was retained after the loss of solvent molecules on heating the material at 200 °C for 2 h, and even after immersion of the crystals in boiling crude oil for several hours.

Given the structural and thermal stability of the SMTP-1 framework, three features of our new functional molecular sieve could potentially be exploited. The unusual windows with both hydrophobic and hydrophilic properties provide new possibilities for shape-selective molecular sieves. They can restrict the size and shape of molecules that are sorbed or desorbed, and large molecules may be flattened to pass through the window. Moreover, the extra-cage could provide space for the formation of bulky intermediates in a catalytic reaction, and the nitrogen atoms of the pendant pyridine rings might serve as coordination sites for intercalation.[14]

This study suggests that a large family of metalloporphyrinate structures might exist that have yet to be synthesized. Some phases possessing unusual pore openings should be accessible by hydrothermal synthesis. Investigations of the organic-functionalized SMTP-1 as a shape-selective catalyst are in progress.[15]

Experimental Section

1: A mixture of $CoCl_2 \cdot 2H_2O$ (0.2384 g), H_2tpyp (0.1243 g), aqueous CsOH (0.3 mL, 50 wt %), CH_3COOH (4 mL), and H_2O (4 mL) was sealed in a 23-mL Teflon-lined stainless autoclave, heated to 200 °C for 48 h, and cooled to 70 °C at 9 K h^{-1}. Needle-shaped purple crystals were filtered off and washed with methanol. Monophase crystalline material was confirmed by X-ray powder diffraction. The yield of crystalline material was 85 % (0.1416 g) based on tpyp, and the synthesis was highly reproducible. Elemental analysis (%): calcd: C 63.54, N 13.48, H 3.88; found: C 63.98, N 14.93, H 4.08.

2: A mixture of $MnCl_2 \cdot 2H_2O$ (0.1719 g), H_2tpyp (0.1171), aqueous CsOH (0.3 mL, 50 wt %), and H_2O (10 mL) was sealed in a 23-mL Teflon-lined stainless autoclave, heated to 200 °C for 48 h, and cooled to 70 °C at 9 °C h^{-1}. Needle-shaped purple crystals (yield 5 %) were accompanied by unidentified brown materials. Elemental analysis: calcd: C 56.41, N 13.16, H 7.10; found: C 56.97, N 13.20, H 3.26.

3: A mixture of $MnCl_2 \cdot 2H_2O$ (0.0839 g,), H_2tpyp (0.1219 g), aqueous CsOH (0.3 mL, 50 wt %), C_2H_5OH (4 mL), and H_2O (4 mL) was sealed in a 23-mL Teflon-lined stainless autoclave, heated to 200 °C for 48 h, and cooled to 70 °C at 9 K h^{-1}. Needle-shaped purple crystals were filtered off and washed with methanol. Monophase crystalline material was confirmed by X-ray powder diffraction. The yield of crystalline material was 86 % (0.1385 g) based on tpyp, and the synthesis was highly reproducible. Elemental analysis (%): calcd: C 63.54, N 13.48, H 3.88; found: C 63.98, N 14.93, H 4.08.

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