An Open-Framework Material with Dangling Organic Functional Groups in 24-Ring Channels

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Open-framework and microporous materials have attracted a lot of attention recently due to their traditional use in catalysis, separation, and ion-exchange and their expected future use as hybrid composite materials in electrooptical and sensing applications.[1] Since the initial discovery of $AlPO_4$-type materials by Flanigen and co-workers, much of the synthesis has focused on metal phosphates with pure inorganic frameworks.[2] An important synthetic principle established by the exploration of this class of materials is that open-framework structures can be configured during synthesis by the charge-matching of inorganic or organic cationic species with suitable ionic framework precursor species.[3] This approach has been particularly effective in the rational design and synthesis of transition metal phosphates and main group metal oxides.[3]

In contrast, although notable progress has been made in the construction of coordination polymers,[4] relatively less progress has been achieved in the synthesis of open-framework materials with organic building blocks using charge-compensating cations.[1] Introducing organic building blocks into the framework, and more desirably, dangling organic functional groups from the framework walls into the porous channels is ideal for generating porous materials with novel molecular recognition properties and chemical reactivities. However, the generation of such structures poses a significant synthetic challenge due to the high coordination tendency and flexibility of organic functionalities. Herein, we report an example of an open-framework material with dangling carboxylic functional groups in 24-ring channels.

The title compound was synthesized by preparing a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (1.61 g), $H_2O_3PCH_2COOH$ (0.532 g), 1,3,5-benzenetricarboxylic acid (BTC, 0.806 g), H_2O (4.00 g), ethylene glycol (15.99 g), and ethylendiamine (0.848 g). The mixture had a pH of 6.19 and was heated in a Teflon-coated steel autoclave at 170 °C for 5 days.[5] The product consisted of thin, needle-shaped crystals with a typical diameter around 10 μm. The optical examination, combined with X-ray powder diffraction, suggests that no other crystalline phase was present. One crystal was used for single-crystal analysis on a SMART CCD diffractometer at room temperature.[6]

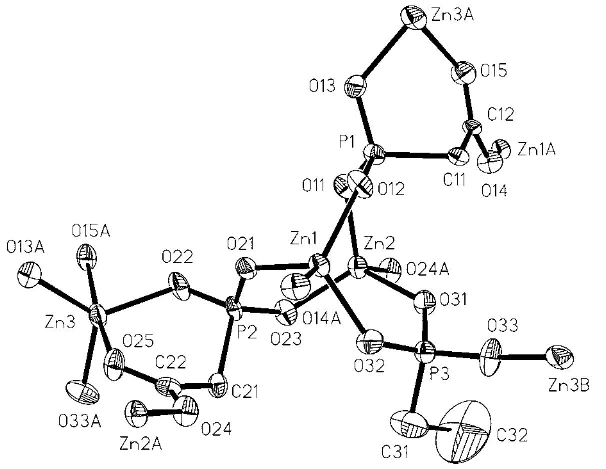

Figure 1. The ORTEP view of coordination environments for Zn, P, and O atoms in the asymmetric unit. Atom labels having "A" or "B" refer to symmetry-generated atoms. Two oxygen atoms of one of the carboxylic group (C32) are not located due to their large positional freedom within 24-ring channels.

The framework is constructed from Zn and one of the organic species ($H_2O_3PCH_2COOH$), and can be described as an interrupted tetrahedral zeolite-type structure. It is built from three unique Zn^{2+} sites, two $O_3PCH_2COO^{3-}$ groups, one $O_3PCH_2COOH^{2-}$ group (Figure 1). All five terminal oxygen atoms in two $O_3PCH_2COO^{3-}$ groups are utilized to connect Zn^{2+} sites. However, one oxygen atom in each $-PO_3$ group and one oxygen atom in the $-COO$ group are bonded to the same zinc site (Zn3, Figure 1). Such a configuration is favorable because of the formation of stable six-atom rings (P−O−Zn−O−C−C). Therefore, each O_3PCH_2COO group in effect behaves like a regular PO_4^{3-} group in zeolite-type frameworks and is 4-connected to four zinc sites. Correspondingly, two of the three unique Zn sites are also 4-connected to phosphorus sites.

The third Zn^{2+} site, even though penta-coordinated to five oxygen atoms, is effectively 3-connected to phosphorus sites because two pairs of oxygen atoms are chelating oxygen atoms from two O_3PCH_2COO groups. To maintain a Zn /P ratio of 1, the O_3PCH_2COOH group is also 3-connected to the framework Zn^{2+} centers, and the dangling -CH_2COOH groups line the wall of 24-ring channels (Figure 2).[7]

It is of interest to note that the structure-directing agents, diprotonated ethylenediamine molecules in this case, are not located at the center of the 24-ring channels, but instead are within the wall that separates the 24-ring channels. Ethylenediamine molecules are completely ordered into a *trans*-conformation. Their two terminal amino groups are expected to form hydrogen bonds with framework oxygen atoms, as suggested by the close N- - -O contacts. The two shortest distances are 3.02(2) Å and 3.02(2) Å at one side (N2) and 2.81(2) Å and 2.86(2) Å at the other end (N1).

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(1) For a recent review on the synthesis of open-framework materials, see: Cheetham, A. K.; Ferey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.

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(3) See, for example: (a) Bu, X.; Feng, P.; Gier, T. E.; Zhao, D.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 13389. (b) Bu, X.; Feng, P.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 11204. (c) Gier, T. E.; Bu, X.; Feng, P.; Stucky, G. D. *Nature* **1998**, *395*, 154. (d) Bu, X.; Feng, P.; Stucky, G. D. *Science* **1997**, *278*, 2080. (e) Feng, P.; Bu, X.; Stucky, G. D. *Nature* **1997**, *388*, 735. (f) Feng, P.; Bu, X.; Tolbert, S. H.; Stucky, G. D. *J. Am. Chem. Soc.* **1997**, *119*, 2497. (g) Gier, T. E.; Bu, X.; Wang, S.; Stucky, G. D. *J. Am. Chem. Soc.* **1996**, *118*, 3039. (h) Feng, P.; Bu, X.; Stucky, G. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1745.

(4) For a recent review on the synthesis of inorganic coordination polymers, see: Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(5) It should be noted that the pH measured in the partially nonaqueous environment may not be directly comparable to that measured in water.

(6) Crystal data for $Zn_3(O_3PCH_2COO)_2(O_3PCH_2COOH)(NH_3CH_2CH_2NH_3)$-(BTC): space group *R*-3 (no. 148), $Z = 18$, Mo K_α radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 45°$, $a = 41.663(7)$ Å, $c = 7.843(2)$ Å, $V = 11790(4)$ Å^3, 0.27 × 0.013 × 0.013 mm, refinement on F^2, $R(F) = 7.43\%$, $wR(F^2) = 19.7\%$, GOF = 1.44 for 265 parameters and 3409 unique reflections with $I > 2.0\sigma(I)$.

(7) For inorganic metal phosphates with 24-ring windows, see: (a) Yang, G.; Sevov, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 8389. (b) Guillou, N.; Gao, Q.; Nogues, M.; Morris, R. E.; Hervieu, M.; Ferey G.; Cheetham, A. K. *C. R. Acad. Sci. II C.* **1999**, *2*, 387. For an interesting open-framework structure templated with long-chain alkyl diamines, see: (c) Sassoye, C.; Loiseau, T.; Taulelle, F.; Ferey, G. *J. Chem. Soc., Chem. Commun.* **2000**, 943.

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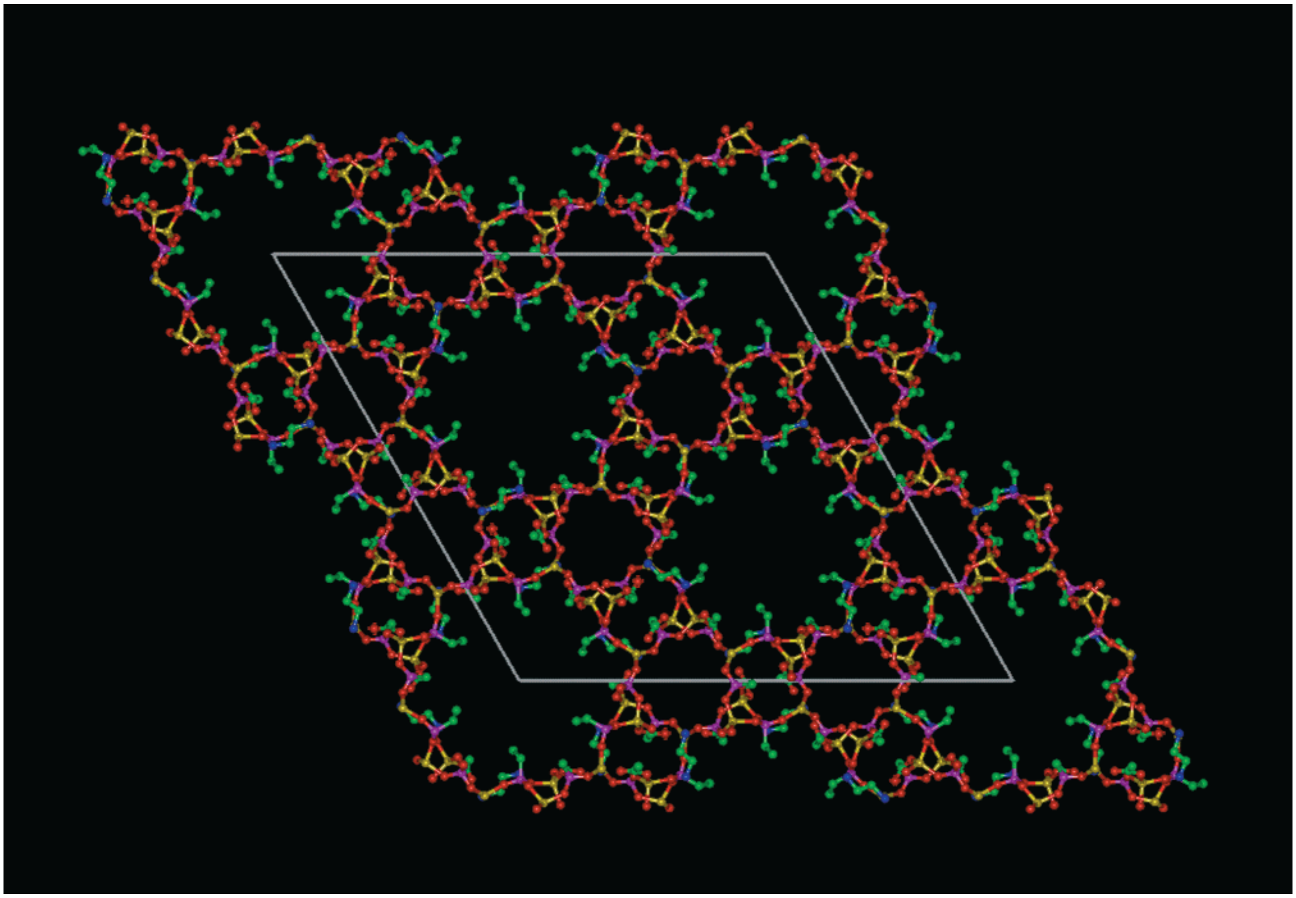

Figure 2. A unit cell packing diagram viewed down the *c* axis showing the location of different species and 24-ring channels. Red: oxygen; yellow: zinc; purple: phosphorus; green: carbon; blue: nitrogen.

The dangling carboxylic group has a high positional freedom, and atomic positions for two oxygen atoms are not well defined. The residual electron density peaks are mainly distributed around the disordered carboxylic groups and at the center of 12-ring channels. The electron density peaks around the center of 12-ring channels are likely those of disordered BTC molecules. The presence of BTC molecules is also suggested by the thermogravimetric analysis that showed a significant weight loss of 48.4% (calcd weight loss based on one BTC molecule per formula unit: 48.1%) between 200 and 780 °C. A control experiment carried out without the addition of BTC (same quantities of the rest of the components) did not generate the same phase based on the powder X-ray diffraction. To further probe the effect of BTC and the role of the carboxylates in the synthesis, three different carboxylic acids were used in the reaction mixture: 1,2,4,5-benzenetetracarboxylic acid, *cis*-1,2-cyclohexanedicarboxylic acid, and *cis*-1,3,5-cyclohexanetricarboxylic acid. All of these carboxylic acids led to the formation of the 24-ring framework reported here.

The synthesis of the title compound provides an interesting example of the use of the charge-compensating principle in generating novel open-framework structures containing functional organic units. Although there are already some open-framework materials with phosphonates,[8] carboxylates,[9] phosphonate-carboxylates[10] in the literature, many of these are based on coordination principles. In addition to the ultra-large pore size (24-ring windows), the title compound also contains 12- and 8-ring channels parallel to the 24-ring channels. Three types of parallel channels form hexagonal, honeycomb arrays. The title compound is a rare example of an open-framework material with dangling carboxylic functional groups uniformly distributed in the channel. The structure-directing reagent/charge-balancing cation is located along the 24-ring framework metal sites, leaving centers of the channels surrounded by organic functional groups. This may allow organic functional group accessible for further chemical manipulation.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic thermal parameters and figures of X-ray powder diffraction pattern and simulated X-ray powder diffraction pattern (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) For example: (a) Johnson, J. W.; Jacobson, A. J.; Butler, W. M.; Rosenthal, S. E.; Brody, J. F.; Lewandowski, *J. Am. Chem. Soc.* **1989**, *111*, 381. (b) LaDuca, R.; Rose, D.; DeBord, J. R. D.; Haushalter, R. C.; O'Conner, C. J.; Zubieta, J. *J. Solid State Chem.* **1996**, *123*, 408. (c) Riou, D.; Roubeau, O.; Ferey, G. *Microporous Mesoporous Mater.* **1998**, *23*, 23. (d) Serpaggi, F.; Ferey, G. *J. Mater. Chem.* **1998**, *8*, 2749. (e) Lohse, D. L.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1619. (f) LeBideau, J.; Payen, C.; Palvadeau, P.; Bujoli, B. *Inorg. Chem.* **1994**, *33*, 4885. (g) Drumel, S.; Janvier, P.; Deniaud, D.; Bujoli, B. *J. Chem. Soc., Chem. Commun.* **1995**, 1051. (h) Maeda, K.; Akimoto, J.; Kiyozumi, Y.; Mizukami, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1033.

(9) For most notable examples, see: (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Eddaoudi, M.; Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391. (c. Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (d) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148. (e) Serpaggi, F.; Ferey, G. *J. Mater. Chem.* **1998**, *8*, 2737.

(10) For the first phosphonate-carboxylate with an extended three-dimensional structure, see: Distler, A.; Sevov, S. C. *J. Chem. Soc., Chem. Commun.* **1998**, 959. For a layered phosphonate-carboxylate, see: Fredoueil, F.; Massiot, D.; Poojary, D.; Bujoli-Doeuff, M.; Clearfield, A.; Bujoli, B. *J. Chem. Soc., Chem. Commun.* **1998**, 175.