JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

A Cubic, 12-Connected, Microporous Metal−Organometallic Phosphate Framework Sustained by Truncated Tetrahedral Nodes

Sayon A. Kumalah Robinson,[†] Marion-Vincent L. Mempin,[†] Amy J. Cairns,[‡] and K. Travis Holman*,[†]

[†]Department of Chemistry, Georgetown University, Washington, D.C. 20057, United States
[‡]Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States

S Supporting Information

ABSTRACT: A rare example of a microporous metal−organic phosphate, $[Co_{12}(\mathbf{L})_6(\mu_3\text{-}PO_4)_4(\mu_3\text{-}F)_4(\mu\text{-}H_2O)_6][NO_3]_2$ (**1**), is synthesized by the reaction of a $[(\eta^5\text{-}C_5H_5)Fe^{II}]^+$-functionalized terephthalate ligand with $Co(NO_3)_2 \cdot 6H_2O$ and phosphate and fluoride ions generated from the *in situ* hydrolysis of hexafluorophosphate. **1** is a cubic, 12-connected, face-centered cubic framework sustained by the linear connection of unprecedented, dodecanuclear truncated tetrahedral coordination clusters.

Coordination polymers[1] or metal−organic frameworks (MOFs)[2] have, for some years now, been at the forefront in the discovery of new materials with applications dependent upon the exhibition of porosity. In this respect, aryl carboxylate ligands, and particularly congeners of 1,3-[3] and 1,4-benzenedicarboxylate (BDC) ligands, have played a central role in MOF compositions, functioning as rigid, extending connectors between metal−ligand coordination clusters that serve as framework nodes. 1,4-BDC congeners alone have yielded a variety of porous organic−inorganic hybrid materials, including $M_2(BDC)_2$,[4] MOF-5 and its modified forms,[5] some of the MIL frameworks (e.g., MIL-53, -68, -71, -85, -88B, -101, and -125),[6] CAU-1,[7] and UiO-66.[8] The structural diversity of microporous coordination polymers can therefore be attributed in large part to the diversity of coordination clusters that may be linked by simple ligands, and the role of serendipity in this sense remains an important one.

Considering the prominent role of metal phosphates (e.g., aluminum, gallium, nickel, and cobalt phosphates)[9−11] as inorganic microporous materials, and the existence of several microporous inorganic−organic metal phosphonates,[12] it is perhaps surprising that microporous metal−organic phosphates (MOPs)—based upon a mix of organic and phosphate ligands—are rare, even though nonporous examples of MOPs are now quite prevalent. Indeed, to our knowledge, the only two microporous MOPs are those reported by Wang and co-workers, namely the anionic zinc(II) phosphate terephthalate or 1,2,4,5-benzenetetracarboxylate frameworks NTHU-2[13] and NTHU-8,[14] respectively. A principal synthetic challenge in achieving porosity in MOPs appears to be one of charge balance. In general, organic countercations, serving also as structure directing agents, must be successfully removed by calcination to impart porosity. Such is the case for NTHU-2 and NTHU-8, with calcination of the organic components giving rise to materials with modest micropore surface areas (112 m^2/g and 250 m^2/g, BET) and bimodal micro/meso-porosities that are not easily reconciled with their original structures.

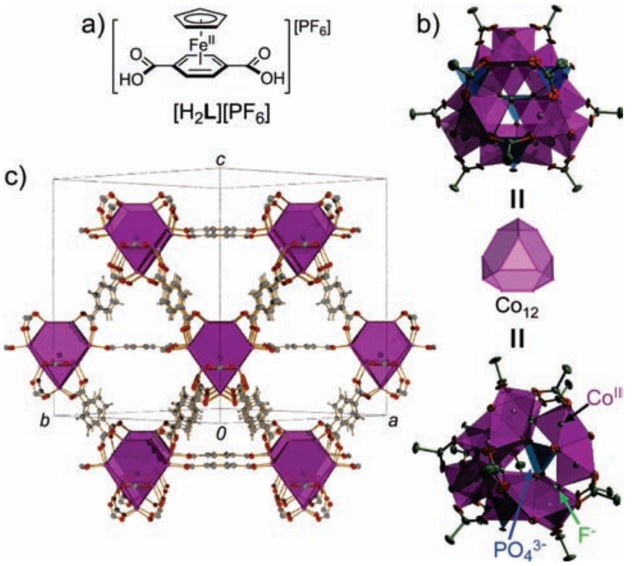

Figure 1. (a) Structure of $[H_2\mathbf{L}][PF_6]$. (b) Polyhedral/thermal ellipsoid and schematic representations of the $[Co_{12}(\mu\text{-}RCO_2)_{12}(\mu_3\text{-}PO_4)_4(\mu_3\text{-}F)_4(\mu\text{-}H_2O)_6]^{4-}$ truncated tetrahedral nodes (Co_{12}) in the crystal structure of **1**. (c) The 12-connected cubic framework structure of **1** as viewed down the interconnected series of ⟨110⟩ directed pores. The appended $[(\eta^5\text{-}C_5H_5)Fe^{II}]^+$ moieties have been omitted for clarity.

We have been exploring stable and readily available organometallic sandwich compounds of arylcarboxylates[15] as ligands in the synthesis of metal-organometallic framework materials (MOMFs),[5c,16] the somewhat unusual feature of MOMFs being that they are sustained by ligands possessing a metal−carbon bond that does not participate in the connectivity of the framework. The $[(\eta^5\text{-}C_5H_5)Fe^{II}]^+$-functionalized BDC ligand $\mathbf{L}^-$ (Figure 1a), for instance, yielded 3D MOMFs α/β-$[M^{II}_3(\mathbf{L})_4(H_2O)_2(\mu\text{-}H_2O)_2][NO_3]_2$ (M = Co, Ni; α/β-GU-MOMF-1 and −2, respectively) that exhibit polymorphism and solvated pore structures that depend upon the relative positioning of the appended $[CpFe]^+$ (i.e., $[(\eta^5\text{-}C_5H_5)Fe^{II}]^+$) moieties.[15] Reported herein is a rare example of a microporous MOP, namely $[Co_{12}(\mathbf{L})_6(\mu_3\text{-}PO_4)_4(\mu_3\text{-}F)_4(\mu\text{-}H_2O)_6][NO_3]_2$, hereafter **1** or GU-MOMF-3. **1** also adopts a rare topology for MOFs, being a cubic, 12-connected ***fcu*** net[17] that is sustained by the linking of unprecedented dodecanuclear nodes by $\mathbf{L}^-$ ligands. Since the

Received: October 1, 2010
Published: January 19, 2011

organometallic $[CpFe]^+$ appendages play no role in defining the connectivity of the framework, **1** can be considered a conceptual prototype for a series of microporous MOPs with potentially tunable pores.

Reaction of excess ethanolic $Co(NO_3)_2 \cdot 6H_2O$ with $[HL \cdot H_2L][PF_6]$[15]—the 1:1 cocrystal of monoprotonated, zwitterionic HL and the $[PF_6]^-$ salt of the doubly protonated $[H_2L]^+$—in a sealed vessel at 120 °C yielded two distinct crystalline materials: dark pink cubic crystals of **1**·solvent, and orange needles, which are free of phosphate and are structurally analogous to the MIL-88B family of MOFs.[6] Clearly, under the conditions of the synthesis, the hexafluorophosphate ions are hydrolyzed to phosphate and fluoride and are subsequently incorporated into **1** in an example of *in situ* ligand synthesis.[18] Some of us have earlier exploited *in situ* $[PF_6]^-$ hydrolysis in the synthesis of a new uranium phosphate.[19] As the starting material is deficient in phosphorus ($L^-/P = 2{:}1$) relative to **1**·solvent ($L^-/P = 1{:}1$), the synthesis of **1** was optimized by introducing $[NH_4][PF_6]$, the reaction under these conditions yielding only single crystalline **1**·solvent (42% isolated yield based on L^-) and a finely powdered, poorly crystalline cobalt phosphate. Notably, and possibly owing to the insolubility of cobalt phosphates, attempts to synthesize **1** from more traditional phosphate and fluoride sources (e.g., $Co_3(PO_4)_2 \cdot H_2O$ or $Co(NO_3)_2 \cdot 6H_2O/H_3PO_4$, and HF) have so far been unsuccessful, yielding only inorganic phases or the MIL-88B-type material. Additionally, attempts to prepare analogs of **1** from other metal(II) ions (e.g., Zn(II)) have so far been unsuccessful.

X-ray single crystal structure analysis of cubic **1**·solvent[20] reveals high symmetry (T_d), dodecanuclear (Co_{12}) coordination clusters assembled from twelve octahedral Co^{II} ions and mixed carboxylate, phosphate, fluoride and aqua ligands (Figure 1b). The Co_{12} clusters have composition $[Co_{12}(\mu\text{-}RCO_2)_{12}(\mu_3\text{-}PO_4)_4(\mu_3\text{-}F)_4(\mu\text{-}H_2O)_6]^{4+}$ and are constructed of twelve CoO_5F octahedra (magenta) and four phosphate tetrahedra (blue), the former arising from the coordination of two separate carboxylate ligands (Co—O = 2.028(4) Å), two separate phosphate oxygens (Co—O = 2.127(4) Å), one H_2O ligand (Co—O = 2.160(6) Å), and a fluoride (Co—F = 2.030(2) Å). Bond Valence Sum analysis confirms the Co^{II} oxidation state.[21] Each CoO_5F octahedron is face-shared with another via phosphate and aqua oxygen atoms, corner shared to two others via the μ_3-fluoride, and further corner shared to two phosphate tetrahedra. The unprecedented Co_{12} cluster is best described as a nonuniform truncated tetrahedron of cobalt ions with Co···Co distances measuring 3.50 Å around the four regular triangular faces and alternating between 3.50 and 2.88 Å along the four irregular hexagonal faces.

The twelve bridging L^- ligands connect the Co_{12} nodes via linear extensions of the triangular edges, generating an open, 12-connected network of face-centered cubic (***fcu***)[17] topology akin to that adopted by cubic-close-packed spheres (Figure 2c) and analogous to the zirconium terephthalate UiO-66.[8] Notably, although high connectivity MOFs are important,[22] 12-connected MOFs are uncommon[3b,7,8,23] and the ***fcu*** topology represents the highest possible connectivity and only possible topology for a (quasi)regular 12-connected net. Moreover, MOFs of ***fcu*** topology have only been previously assembled by the linking of cuboctahedral nodes,[3b,23a−23c] and, curiously, it appears to be generally less well recognized that the edge-sharing of truncated tetrahedra will also generate an ***fcu*** net. Of course, the truncated tetrahedral Co_{12} node can also be thought of as a highly tetrahedrally *distorted* pseudocuboctahedron where the carboxylate carbon atoms of the ligand represent the vertices.

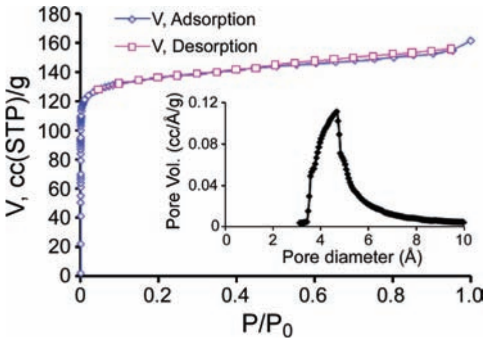

Figure 2. Low temperature (77 K) N_2 sorption and desorption isotherms for **1** and (inset) corresponding Hovarth-Kawazoe pore size analysis.

It is important to recognize that the Co_{12} nodes of **1** are formally anionic, as would be the framework (like in most other MOPs) were it not for the covalent appendage of the positively charged $[CpFe]^+$ moieties to the BDC^{2-} portions of L^-. Instead, because of the metal—ligand stoichiometry, the overall framework of **1** is positively charged and requires the incorporation of a *sub*stoichiometric number of anions relative to the Co_{12} nodes, which necessitates, therefore, the formation of cavities/pores to be occupied by solvents. We believe this is a generally important feature of zwitterionic ligands such as L^-; charge balance and ligand size considerations are dramatically affected by the presence of the "spectator" moiety, in this case $[CpFe]^+$.

Of course, being an ***fcu*** net, **1** inherently features octahedral and tetrahedral holes that are connected via a 3D network of pores. The pores and holes in **1**·solvent are occupied by highly disordered counteranions and/or solvent that could not be crystallographically identified. SQUEEZE analysis[21] of the nonframework portion of **1**·solvent indicates that, even with the relatively bulky $[CpFe]^+$ residues, the pores constitute approximately 33% (~4620 Å^3) of the **1**·solvent unit cell volume, corresponding to a calculated pore volume of 0.224 cm^3/g in **1**. The large available volume suggests that **1** could accommodate 13—15 molecules of ethanol, or up to 37 molecules of water per formula unit, after accounting for the volume occupied by the nitrate counterions.[21] SQUEEZE, however, estimates only 137 e$^-$ per formula unit to be attributable to the solvent and counterions, corresponding to ca. three molecules of ethanol ($2[NO_3]^- + 3EtOH = 142\ e^-$) in the single crystal structure of **1**·solvent. ^1H NMR analysis of D_2O-digested single crystals of **1**·solvent suggests the presence of at least five ethanol molecules per formula unit whereas thermal gravimetric analysis (TGA) shows a mass loss from room temperature to 50 °C (11.2%) that is appreciably greater than that expected for 3—5 ethanols. Thus, the solvent composition of crystalline **1**·solvent is likely a mixture of ethanol and water molecules with a variable composition associated with facile solvent loss at or near room temperature. It has also been difficult to accurately quantify the fluoride content of bulk **1**. The ^{19}F NMR spectrum of the above NMR sample, with CF_3CH_2OH as an internal concentration standard, exhibits a single peak at −150 ppm corresponding to fluoride, but suggests only three fluorides per formula unit (vs expected four). Combustion analyses of **1** gave inconsistent results with respect to fluorine content.[21]

The bulk of the solvent accessible volume in **1** lies within the octahedral-like holes of the ***fcu*** framework, each of which (four per unit cell) has an approximate volume of ~950 Å^3. The $[CpFe]^+$ moieties of the L^- ligands are directed into the tetrahedral holes but are statistically disordered (∼4:1) about the two faces of the BDC^{2-} rings such that there exists two types of tetrahedral cavities. The cavities are delimited by six $\mathbf{L}^-$ ligands and so half are occupied by, on average, 80% of the six possible $[CpFe]^+$ moieties and the other half are occupied by, on average, 20% of six possible $[CpFe]^+$ moieties. Clearly, disorder of the $[CpFe]^+$ moieties leads to nonuniform pore structure. Interestingly, at putative sites in the crystal where all six $[CpFe]^+$ moieties are directed into a tetrahedral hole, a small, discrete, seemingly inaccessible cavity (62 Å^3) is formed.

As suggested by TGA, **1**·solvent can be desolvated under very mild conditions—simply by heating to 50 °C under vacuum for 24 h. The microporosity of the resultant empty **1** was confirmed by low pressure N_2 sorption isotherms collected at 77 K (Figure 2). The experimental BET surface area measured on multiple samples consistently measured 441(9) m^2/g (613(3) m^2/g Langmuir) and the micropore volume was determined to be 0.209(1) cm^3/g by fitting the isotherm data to a Horvath–Kawazoe (H–K) plot. Thus, the experimental H–K pore volume agrees well with the solvent accessible volume calculated by SQUEEZE (0.224 cm^3/g) for the single crystal structure of **1**·solvent. The H–K micropore diameters are also consistent with the crystal structure (Figure 2, inset; Figures S8 and S9, Supporting Information). Taken together, the sorption data suggests that **1** maintains its framework structure upon desolvation. This fact was further demonstrated by determination of the unit cell of both single crystals and bulk powdered **1** *after* N_2 sorption analysis, confirming unequivocally the microporous nature of **1**. H_2 sorption data were also acquired at 77 K and indicated that **1** was able to absorb just over 1 wt % of H_2 at 1 bar (Figure S6, Supporting Information).[21]

In summary, **1** constitutes only the third example of a microporous metal–organic phosphate, one that can be emptied under mild conditions and exhibits a rigid, porous framework essentially identical to its as-synthesized form. The dodecanuclear, truncated tetrahedral coordination clusters in **1** are unprecedented and may constitute a general means by which one could achieve an isoreticular[2a] family of ***fcu*** frameworks (or others) using other bridging carboxylate ligands. It may be possible, for instance, to synthesize analogs of **1** from other zwitterionic, monoanionic dicarboxylates or simple dicarboxylates in the presence of other cations. Alternatively, **1**, or its plausible $[CpRu]^+$-functionalized analogue, may be active toward photochemical displacement of some or all of the $[CpM]^+$ ($M = Fe^{II}, Ru^{II}$) moieties, thereby generating useful organometallic moieties (e.g., $[CpRu(solvent)_3]^+$) within the framework and/or greatly modifying pore characteristics. Indeed, the metallocyclopentadienyl groups of **1** are readily accessible from the ∼1 nm^3 octahedral cavities (Figure S9, Supporting Information) and present opportunities to explore organometallic chemistry within the pores of MOMFs. Progress on these fronts will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details for the synthesis, crystallography, NMR, elemental analysis, TGA, gas sorption. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
kth7@georgetown.edu

■ ACKNOWLEDGMENT

We gratefully acknowledge the U.S. National Science Foundation (DMR-0349316) and Georgetown University for support of this work. We are grateful to Mohamed Eddaoudi for providing access to gas sorption instrumentation.

■ REFERENCES

(1) (a) Robson, R. *Dalton Trans.* **2008**, 5113–5131. (b) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Mater.* **2009**, *1*, 695–704.

(2) (a) Tranchemontagne, D. J.; Mendoza-Cortes, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem Soc. Rev.* **2009**, *38*, 1257–1283. (b) Perry, J. J.; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, *38*, 1400–1417. (c) Macgillivray, L. R. *Metal-Organic Frameworks: Design and Applications*; John Wiley & Sons: New York, 2010.

(3) (a) Yan, Y.; et al. *J. Am. Chem. Soc.* **2010**, *132*, 4092–4094. (b) Cairns, A. J.; Perman, J. A.; Wojtas, L.; Kravtsov, V. C.; Alkordi, M. H.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 1560–1561. (c) Tanaka, D.; Henke, A.; Albrecht, K.; Moeller, M.; Nakagawa, K.; Kitagawa, S.; Groll, J. *Nature Chem.* **2010**, *2*, 410–416.

(4) (a) Mori, W.; Inoue, F.; Yoshida, K.; Nakayama, H.; Takamizawa, S.; Kishita, M. *Chem. Lett.* **1997**, 1219–1220. (b) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571–8572.

(5) (a) Eddaoudi, M.; Li, H. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397. (b) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–472. (c) Kaye, S.; Long, J. *J. Am. Chem. Soc.* **2008**, *130*, 806.

(6) Ferey, G.; Serre, C *Chem. Soc. Rev.* **2009**, *38*, 1380–1399.

(7) Ahnfeld, T.; Guillou, N.; Gunzelmann, D.; Margiolaki, I.; Loiseau, T.; Ferey, G.; Senker, J.; Stock, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 5163–5166.

(8) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.

(9) (a) Feng, P. Y.; Bu, X. H.; Stucky, G. D. *Nature* **1997**, *388*, 735–741. (b) Forster, P. M.; Eckert, J.; Chang, J. S.; Park, S. E.; Ferey, G.; Cheetham, A, K. *J. Am. Chem. Soc.* **2006**, *125*, 1309–1312.

(10) Davis, M. E. *Nature* **2002**, *417*, 813–821.

(11) (a) Natarajan, S.; Mandal, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4798–4828. (b) Cheetham, A. K.; Ferey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268–3292. (c) Murugavel, R.; Choudhury, A.; Walawalkar, M. G.; Pothiraja, R.; Rao, C. N. R. *Chem. Rev.* **2008**, *108*, 3549–3655.

(12) Shimizu, G. K. H.; Vaidhyanathan, R.; Taylor, J. M. *Chem. Soc. Rev.* **2009**, *38*, 1430–1449.

(13) Liao, Y. C.; Liao, F. L.; Chang, W. K.; Wang, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 1320–1321.

(14) Huang, S. H.; Lin, C. H.; Wu, W. C.; Wang, S. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 6124–6127.

(15) Kumalah, S. A.; Holman, K. T. *Inorg. Chem.* **2009**, *48*, 6860–6872.

(16) Oh, M.; Carpenter, G.; Sweigart, D. *Acc. Chem. Res.* **2004**, *37*, 1.

(17) Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr.* **2003**, *A59*, 22–27.

(18) Zhang, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 1201–1219.

(19) Deifel, N. P.; Holman, K. T.; Cahill, C. L. *Chem. Commun.* **2008**, 6037–6038.

(20) Crystal data for **1**·3EtOH, $C_{78}H_{60}O_{46}F_4P_4Co_{12}Fe_6\cdot 3(C_2H_6O)$, $M = 3242.74$, dark pink cube, 0.24 × 0.22 × 0.22 mm^3, cubic, *F*-43*m* (No. 216), $a = 24.1624(9)$ Å, $V = 14106.5(9)$ Å^3, $Z = 4$, $D_c = 1.527$ g/cm^3, $F_{000} = 6256$, Siemens SMART CCD, MoKα radiation, $\lambda = 0.71073$ Å, $T = 173(2)$K, $2\theta_{max} = 50.0°$, 3846 reflections collected, 1258 unique ($R_{int} = 0.0484$). Final $GooF = 1.059$, $R1 = 0.0470$, $wR2 = 0.1339$, R indices based on 1144 reflections with $I > 2\sigma(I)$ (refinement on F^2), 75 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 2.087$ mm^{-1}. $\chi = 0.38(6)$. Structure treated with SQUEEZE (see Supporting Information). CCDC-786043 contains supplementary crystallographic data for this paper.

(21) See Supporting Information.

(22) Hill, R. J.; Long, D. L.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Acc. Chem. Res.* **2005**, *38*, 335–348.

(23) (a) Li, D.; Wu, R.; Zhou, X.-P.; Zhou, R.; Huang, X.-C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4175–4178. (b) Zhang, X.-M.; Fang, R.-Q.; Wu, H.-S. *J. Am. Chem. Soc.* **2005**, *127*, 7670. (c) Jia, J.; Lin, X.; Wilson, C.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Walker, G.; Cussen, E. J.; Schroder, M. *Chem. Commun.* **2007**, 840–842. (d) Sumida, K.; Hill, M. R.; Horike, S.; Dailly, A.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 15120–15121.