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Metal−Organic Polyhedron Based on a Cu^{II} Paddle-Wheel Secondary Building Unit at the Truncated Octahedron Corners

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A metal−organic polyhedron of truncated octahedral geometry augmented with a C_4-symmetric square-planar Cu^{II} paddle-wheel node as a secondary building unit can be prepared using a C_3-symmetric ligand that occupies the face of the octahedral cage, where the three phenyl groups containing a *m*-carboxylate group in the ligand provide the necessary curvature to form the finite octahedral cage.

Bioinspired synthetic highly symmetric metal−organic polyhedra (MOPs) with a variety of symmetries are reported in the literature.[1−3] MOPs find applications in recognition,[4] catalysis,[5] and synthetic membranes for ion channels.[6] The MOPs described in the literature are prepared by two general strategies, either edge-directed self-assembly by the linear components connected at the corners[1] or face-directed facial components linked at the edges[2] or corners.[3] Many MOPs constructed based on the face-directed strategy make use of C_3-symmetric ligands,[2a−e,3b−g] most of which are pyridine-based ligands, as the primary building units.[2a−e,3b−f] Liu and Tong reported that an imidazole-based tridentate face-directed ligand self-assembled to form a MOP of octahedral geometry.[3g] Recently, we reported on a face-driven corner-linked truncated octahedral cage with Pd^{II} coordinated with *m*-pyridyl as well as *p*-pyridyl groups with an amide linkage.[3c]

In addition to the traditional MOPs and metal−organic frameworks (MOFs) of simple metal nodes and organic linkers, augmentation to the MOPs and MOFs using secondary building units (SBUs) such as the tetranuclear $[Zn_4O(COO)_6]$[7] unit as an octahedral node and the dinuclear paddle-wheel $[Cu^{II}(COO)_4]$[1d,8−10] unit as a square node has been investigated. Eddaoudi and co-workers have reported an edge-directed octahedron with 2,5-pyridinedicarboxylic acid, where In^{III} is coordinated with pyridine as well as carboxylate functional groups.[1e] MOPs of various symmetries with a Cu^{II} paddle-wheel SBU[8] in addition to various 2D and 3D MOFs[9,10] have been reported. Yaghi and co-workers

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(1) (a) Caulder, D. L.; Powers, R. E.; Parac, T. N.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 1840–1843. (b) Tominaga, M.; Suzuki, K.; Kawano, M.; Kusukawa, T.; Ozeki, T.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5621–5625. (c) Tominaga, M.; Suzuki, K.; Murase, T.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 11950–11951. (d) Ni, Z.; Yassar, A.; Antoun, T.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 12752–12753. (e) Liu, Y.; Kravtsov, V. C.; Beauchamp, D. A.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2005**, *127*, 7266–7267. (f) Paul, R. L.; Bell, Z. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4883–4888.

(2) (a) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469–471. (b) Takeda, N.; Umemoto, K.; Yamaguchi, K.; Fujita, M. *Nature* **1999**, *398*, 794–796. (c) Umemoto, K.; Yamaguchi, K.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 7150–7151. (d) Umemoto, K.; Tsukui, H.; Kusukawa, T.; Biradha, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2620–2622. (e) Olenyuk, B.; Whiteford, J. A.; Fechtenkotter, A.; Stang, P. J. *Nature* **1999**, *398*, 796–799.

(3) (a) Brückner, C.; Powers, R. E.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 1837–1839. (b) Chand, D. K.; Biradha, K.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *Chem. Commun.* **2002**, 2486–2487. (c) Moon, D.; Kang, S.; Park, J.; Lee, K.; John, R. P.; Won, H.; Seong, G. H.; Kim, Y. S.; Kim, G. H.; Rhee, H.; Lah, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 3530–3531. (d) Park, J.; Hong, S.; Moon, D.; Park, M.; Lee, K.; Kang, S.; Zou, Y.; John, R. P.; Kim, G. H.; Lah, M. S. *Inorg. Chem.* **2007**, *46*, 10208–10213. (e) Ronson, T. K.; Fisher, J.; Harding, L. P.; Hardie, M. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 9086–9088. (f) Hiraoka, S.; Harano, K.; Shiro, M.; Ozawa, Y.; Yasuda, N.; Toriumi, K.; Shionoya, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6488–6491. (g) Liu, H.-K.; Tong, X. *Chem. Commun.* **2002**, 1316–1317. (h) Duriska, M. B.; Neville, S. M.; Moubaraki, B.; Cashion, J. D.; Halder, G. J.; Chapman, K. W.; Balde, C.; Létard, J.-F.; Murray, K. S.; Kepert, C. J.; Batten, S. R. *Angew. Chem., Int. Ed.* DOI:10.1002/anie.200805178.

(4) (a) Tashiro, S.; Tominaga, M.; Kawano, M.; Therrien, B.; Ozki, T.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 4546–4547. (b) Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **2002**, *124*, 13576–13582. (c) Davis, A. V.; Raymond, K. N. *J. Am. Chem. Soc.* **2005**, *127*, 7912–7919.

(5) (a) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Science* **2007**, *316*, 85–88. (b) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 351–360. (c) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251–254. (d) Yoshizawa, M.; Kusukawa, T.; Fujita, M.; Yamaguchi, K. *J. Am. Chem. Soc.* **2000**, *122*, 6311–6312.

(6) Jung, M.; Kim, H.; Baek, K.; Kim, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 5755–5757.

(7) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279. (b) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–472.

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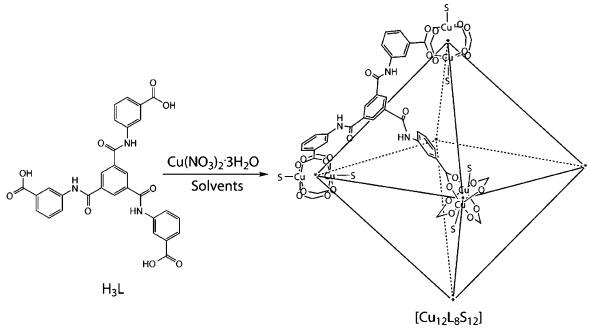
Scheme 1. Self-Assembly of Ligands L^{3-} with Cu^{II} Forming the Octahedral Cage **1**, Where the Corners of the Octahedron Are Augmented Using the Paddle-Wheel SBU, $[Cu_2(COO)_4]$



have reported edge-directed corner-linked truncated octahedra with Cu^{II} paddle-wheel SBUs.[8a] Sun and co-workers have reported a self-assembled octahedral cage with a C_3-symmetric face-directed ligand.[8e] In the crystal structure, however, the octahedral cage has five dinuclear paddle-wheel corners, while the sixth one is a mononuclear corner.

In a continuation of our earlier work,[3c] we have now prepared a self-assembled MOP of a truncated octahedron with 3,3′,3″-[1,3,5-benzenetriyltris(carbonylimino)]tris-(benzoate) (L^{3-}) as a C_3-symmetric face-driven primary building unit with Cu^{II} ions at the square-planar paddle-wheel corners (Scheme 1). The use of a slight excess of copper nitrate combined with the ligand H_3L in a solvent mixture of *N*,*N*′-dimethylacetamide (DMA) and acetonitrile (2:3) at 85 °C yielded light-bluish-green crystals of the metal complex ($[Cu_{12}L_8S_{12}]\cdot xS$ (**1**), where S is either a DMA or water molecule and *x* is the number of solvent molecules in the crystal, after 4 days. Crystal structure analysis revealed that crystal **1** consists of discrete MOPs, each composed of eight C_3-symmetric L^{3-} ligands at the faces connected by six C_4-symmetric copper paddle-wheel connectors at the corners. The ball-and-stick model of the single MOP is shown in Figure 1a. The overall charge of the MOP is neutral. The meta-positioned carboxylate group in the ligand, which forms the copper paddle-wheel SBU, $[Cu_2(COO)_4]$, promotes the essential curvature for the MOP. The ligand occupies the face of the octahedron and forms an augmented, face-driven truncated octahedron. Each Cu^{II} in the paddle-wheel moiety coordinated with one DMA molecule points outward from the octahedral cage. Inside the octahedral cage, the Cu^{II} ion in the paddle-wheel moiety is coordinated to either a water molecule or a partially identified DMA molecule. (The asymmetric unit of **1** is shown in Figure S1 in the Supporting Information.)

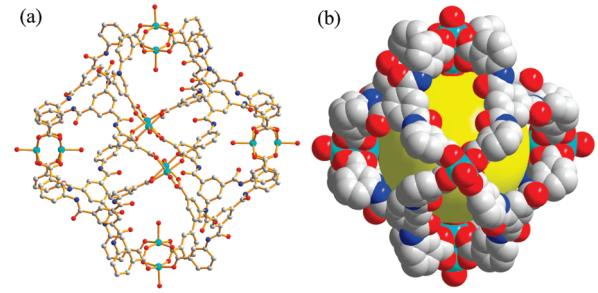


Figure 1. (a) Ball-and-stick model of **1** from crystal structure analysis and (b) CPK presentation of **1**. Hydrogen atoms are omitted for clarity. Only the oxygen atoms of the DMA are shown. The approximate solvent cavity is shown as a large yellow dummy ball.

All of the ligands are oriented in a concave shape in the MOP; the central phenyl ring is oriented mostly parallel with the tangent of the MOP, while all of the carboxylated phenyl rings are oriented perpendicular to the central phenyl ring. The four ligands in the asymmetric unit exist with discrete conformations in terms of the orientation of the amide linkage and the benzene *m*-carboxylate group. According to the orientation of the carbonyl group of the amide linkage and the *m*-carboxylate group, the conformation of the ligand subunits has been classified as anti (both the carbonyl and *m*-carboxylate are oriented in opposite directions), syn (both of the groups are oriented on the same side), and int (the *m*-carboxylate ring is oriented nearly perpendicular to the central phenyl ring) (Scheme S1 in the Supporting Information).[3c,d] The flexible rotation at the amide linkage allows diverse ligand conformations. Only one ligand in the asymmetric unit has all-anti conformations, while the other three have combinations of the above three conformations (Figure S2 in the Supporting Information). The CPK model of the octahedral cage is shown in Figure 1b. The outer diameter of the octahedral cage is nearly 28 Å, and the inner diameter is approximately 17 Å.

In the crystal structure of **1**, the octahedral cages are arranged in a cubic closest packing (CCP) arrangement (Figure 2). Each MOP exhibits hydrogen-bonding interaction with the neighboring six MOPs via the amide groups (Table S2 and Figure S3 in the Supporting Information). Of the 24 amide functional groups in each MOP, only 12 of them are

(8) (a) Eddaoudi, M.; Kim, J.; Wachter, J. B.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4368–4369. (b) Furukawa, J.; Kim, J.; Plass, K. E.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 8398–8399. (c) Ni, Z.; Yassar, A.; Antoun, T.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 12752–12753. (d) Eddaoudi, M.; Kim, J.; Vodak, D.; Sudik, A.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4900–4904. (e) Zhu, H.-F.; Fan, J.; Okamura, T.-A.; Zhang, Z.-H.; Liu, G.-X.; Yu, K.-B.; Sun, W.-Y.; Ueyama, N. *Inorg. Chem.* **2006**, *45*, 3941–3948.

(9) (a) Bourne, S. A.; Lu, J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2111–2113. (b) Xue, D.-X.; Lin, Y.-Y.; Cheng, X.-N.; Chen, X.-M. *Cryst. Growth Des.* **2007**, *7*, 1332–1336. (c) Wang, Z.; Kravtsov, V. Ch.; Walsh, R. B.; Zaworotko, M. J. *Cryst. Growth Des.* **2007**, *7*, 1154–1162. (d) Gao, L.; Zhao, B.; Li, G.; Shi, Z.; Feng, S. *Inorg. Chem. Commun.* **2003**, *6*, 1249–1251. (e) Bodwin, J. J.; Pecoraro, V. L. *Inorg. Chem.* **2000**, *39*, 3434–3435.

(10) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148–1150. (b) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021–1023. (c) Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2002**, *124*, 376–377. (d) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 3896–3897. (e) Wang, X.-S.; Ma, S.; Sun, D.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 16474–16475. (f) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858–1859. (g) Wang, X.-S.; Ma, S.; Forster, M.; Yuan, D.; Eckert, J.; Lopez, J. J.; Murphy, B. J.; Parise, J. B.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 7263–7266. (h) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 1012–1016. (i) Cairns, A. J.; Perman, J. A.; Kravtsov, V. Ch.; Alkordi, M. H.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 1560–1561. (j) Perry, J. J., IV; Kravtsov, V. Ch.; McManus, G. J.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 10076–10077. (k) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, *130*, 1833–1835. (l) Lee, Y.-G.; Moon, H. R.; Cheon, Y. E.; Suh, M. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 7741–7745.

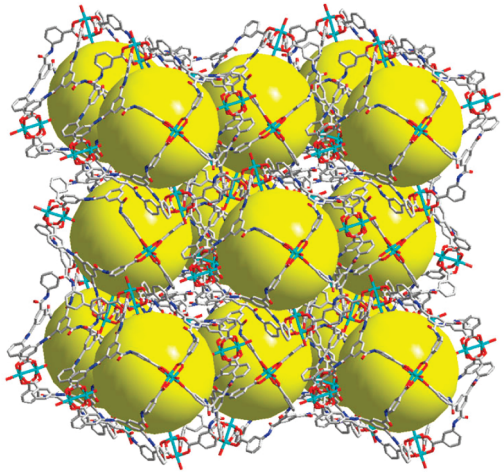


Figure 2. Packing diagram of **1** in a ball-and-stick model of the MOP, with a yellow dummy ball showing the solvent cavity. The octahedral cages in the CCP arrangement are alternatively represented in the form of the face-centered-cubic lattice type.

involved in the N−H···O═C hydrogen-bonding interaction. The remaining six MOPs in the CCP arrangement are involved in van der Waals interactions. The octahedral cages are well packed in the crystal structure; there is not much vacant space outside the octahedral cages (Figure S4 in the Supporting Information). Although each cage has 12 elliptical windows at the edges of the octahedron and the window size is nearly 6.2 Å in width and approximately 10.3 Å in length (Figure S5 in the Supporting Information), all of them are mutually blocked by the neighboring octahedral cages.

The thermal properties of **1** were studied by thermogravimetric analysis (TGA). An air-dried microcrystalline sample was heated to 550 °C (Figure S6a in the Supporting Information). The initial weight loss of approximately 13.2% at 75.6 °C corresponds to a loss of 68 water molecules in the solvent cavity (calcd 13.3%). At 224 °C, 32 coordinated and uncoordinated DMA molecules had been liberated from the crystal, with a large weight loss of nearly 29.8% (calcd 30.0%). Decomposition of the material was observed to take place in two steps from around 250 °C upward, with an overall weight loss of 48.2%. The TGA of **1a**, which was prepared by presoaking **1** in DMA, methanol, and methylene chloride, followed by vacuum-drying at ambient temperature, showed a gradual weight loss of approximately 13.0% up to 219 °C (Figure S6b in the Supporting Information). This weight loss corresponds to a loss of 27 water and 3 DMA molecules (calcd 12.4%), which are probably the ligated solvent molecules and additional water molecules readsorbed from the air.[11] A large weight loss of the material upon decomposition was observed at around 260 °C with a weight loss of 72.2%.

Powder X-ray diffraction (PXRD) analyses were performed on the samples **1**, **1a**, and **1b**, where **1b** was prepared in a manner similar to that of **1a** but with vacuum-drying at 100 °C overnight (Figure S7 in the Supporting Information). The basic features of the PXRD patterns of **1** and **1a** resemble that simulated from the single-crystal structure of **1**.[12] However, the PXRD peaks of **1b** are significantly broadened and weakened, regardless of the sample treatment. This suggests that the sample loses its crystallinity when the solvent is removed from the cavity.

We also studied the stability of **1** in the form of cages in solution. The ^{1}H NMR spectrum of **1** in *N*,*N*′-dimethyl sulfoxide-d_6 (DMSO-d_6) shows the paramagnetic influence of the Cu^{II} ion on the protons of the benzoate phenyl ring (Figure S8 in the Supporting Information). The aromatic proton peaks around 7−8.5 ppm are broadened and the intensity is very weak, which indicates the association of the ligand entangled with the paramagnetic Cu^{II} ion in solution. Atomic force microscopy (AFM) imaging has been used to support the integrity of the cages. A small drop of a dilute solution of **1** in DMSO, which was sonicated and later centrifuged, was placed on a mica sheet and dried. The surface of the sheet was scanned using the AFM scanner in tapping mode. Discrete spherical-shaped cages were observed (Figure S9 in the Supporting Information). The experimentally observed height of the each cage was approximately 1.8 nm, which is smaller than the estimated size of the cage from the crystal structure, namely, ∼2.8 nm. Because the sample was scanned in tapping mode, the cage may undergo ∼35% contraction, caused by the cantilever tip. We observed the same type of effect earlier.[3c] Although **1** showed 52.9% solvent cavity (24 131.7 Å^3 per unit cell)[13] and **1a** maintained its crystallinity, as shown in the PXRD, a preliminary N_2 absorption study on **1a** at 77 K did not show any appreciable gas absorption, probably because of the blockage of the cavity windows in the activated sample.

In summary, the C_3-symmetric ligand composed of *m*-carboxylate groups self-assembled with a Cu^{II} metal ion to form paddle-wheel connecting nodes and resulted in a truncated octahedral cage. The eight ligand molecules occupy faces of the cage. These cages are arranged in CCP arrangement in the crystal. The integrity of the cage structure in solution was verified using NMR and AFM techniques.

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Supporting Information Available: Experimental procedure, crystallographic details and an X-ray crystallographic file in CIF format, TGA data, PXRD data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Elemental analysis also supports the presence of some additional water molecules in **1a**.

(12) Although PXRD of the unground sample gives sharp diffraction peaks, grinding of the same sample leads to severe peak broadening. In order to avoid the peak broadening during the grinding process, the sample was ground with a DMA solvent and then either air-dried or vacuum-dried.

(13) Spek, A. L. *Platon* program (version 1.08). *Acta Crystallogr., Sect. A* **1990**, *46*, 194−201.