

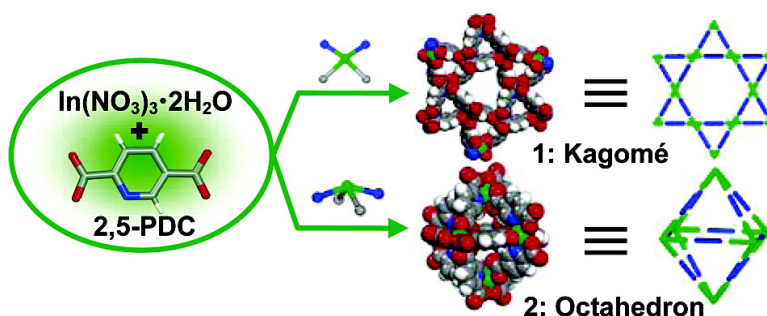
Communication

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## 4-Connected Metal–Organic Assemblies Mediated via Heterochelation and Bridging of Single Metal Ions: Kagomé Lattice and the $M_6L_{12}$ Octahedron

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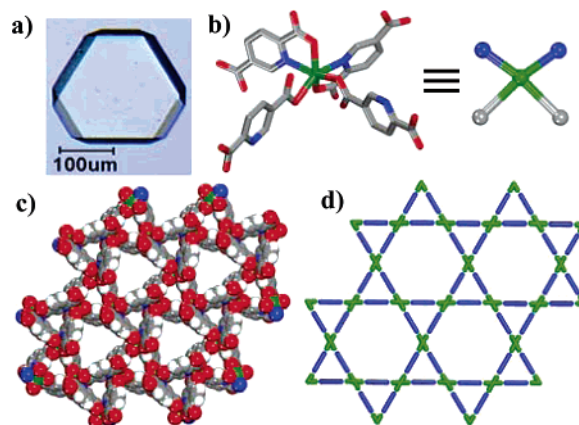
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Increasing desire to design functional solid-state materials has promoted the search for and development of new synthetic strategies as a means to tune and/or enhance the respective properties.<sup>1</sup> The molecular building block (MBB) approach has emerged as a suitable route toward the construction of such materials.<sup>2</sup> Metal–ligand-directed assembly, using the MBB approach, has shown promise toward the logical design and synthesis of a class of functional materials known as metal–organic assemblies.<sup>3</sup> Nevertheless, flexible MBBs based on single metal ions<sup>4</sup> do not promote the rational design of atypical metal–organic assemblies unless the rigidity and directionality have been introduced through control of the geometry and angles within the metal coordination sphere. Accordingly, in addition to the bridging functionality and the necessary rigidity of the ligand, its ability to saturate the coordination sphere of the selected metal and induce directionality is ideal. Our approach has been to render each heterocoordinated single metal ion, formed in situ, rigid and directional using ligands that permit the completion of the metal ion coordination sphere via a heterochelating functionality. Recently, we successfully employed this novel strategy in the design and synthesis of a metal–organic cube based on bridging 3-connected building units,  $MN_3O_3$ , where the metal–nitrogen bonds direct the topology while the  $\alpha$ -carboxylate oxygen atoms complete the octahedral coordination sphere of the metal and lock it into its position through the formation of three rigid five-membered rings via N- and O-chelation.<sup>5</sup>

Here, we report the expansion of this approach to other MBBs, namely  $MN_2(CO_2)_4$  (containing two N- and O-chelating moieties and two bridging carboxylates at the remaining open metal sites; Figure 1b), permitting the formation, in situ, of 4-connected building units. Their assembly with 2,5-pyridinedicarboxylic acid (2,5- $H_2$ -PDC), a ligand containing concurrently the chelating and bridging functionality, has permitted the construction of two supramolecular isomers based on 4-connected vertexes, namely a metal–organic octahedron,  $M_6L_{12}$ , and a 2-D metal–organic framework having a Kagomé topology.

Reaction between 2,5- $H_2$ PDC and  $In(NO_3)_3 \cdot 2H_2O$  in an EtOH/ $H_2O$  solution in the presence of 4,4'-trimethylenedipiperidine (TMDP) yields a homogeneous microcrystalline material.<sup>6</sup> The synthesized compound was characterized and formulated by elemental microanalysis and single-crystal X-ray diffraction studies as  $In(2,5-PDC)_2(HTMDP)(EtOH)(H_2O)_2$  (**1**).<sup>7</sup> The purity of **1** was confirmed by similarities between simulated and experimental X-ray powder diffraction (XRPD) (see Supporting Information Figure S1). In the crystal structure of **1** (Figure 1), each indium metal ion is coordinated to two nitrogen atoms and four oxygen atoms of four independent 2,5-PDC ligands, respectively, to form an octahedral surrounding  $In(III)$  in the MBB,  $InN_2(CO_2)_4$ . Each independent 2,5-



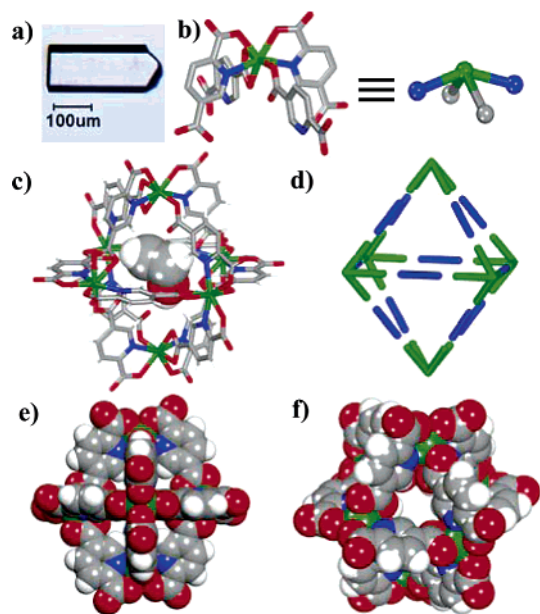
**Figure 1.** (a) Optical image of **1**. X-ray crystal structure of **1**: (b) illustration of indium MBB,  $InN_2(CO_2)_4$ , which can be viewed as a 4-connected node, *cis*- $InN_2(CO_2)_2$ , (c) space-filling representation of a 2-D Kagomé layer (color scheme: carbon = gray, hydrogen = white, nitrogen = blue, oxygen = red, indium = green), and (d) a schematic representation of the Kagomé lattice.

PDC is coordinated to two  $In(III)$  metals by forming a five-membered ring via N- and O-heterochelation, and in a monodentate fashion through the carboxylate in the 5-position.  $InN_2(CO_2)_4$ , where the  $In-N$  bonds and  $In-(5\text{-carboxylate})$  bonds direct the topology (positioning each  $In$  at  $120^\circ$  vis-à-vis 2,5-PDC) and the  $\alpha$ -carboxylate oxygens merely complete the  $In(III)$  coordination sphere, can be regarded as a quasi-planar 4-connected building unit, *cis*- $InN_2(CO_2)_2$  (Figure 1b). The assembly of the 4-connected nodes results in the generation of three- and six-membered windows to give an overall Kagomé lattice topology. The anionic layers stack in an ABCDEF fashion, the interlayer separation of 8.585 Å equals  $1/6$  of the longest unit cell parameter, to create a honeycomb-like pattern with hourglass-shaped channels along [001] with a diameter variation in the range ca. 0.5–1.2 nm (see Supporting Information Figure S2). The disordered interlayer HTMDP cations are located in the wider areas of the channel, hexagonal cavities, and point toward the trigonal windows. To our knowledge, metal–organic frameworks with Kagomé lattice topology are scarce,<sup>8</sup> even though inorganic Kagomé compounds are relatively abundant.<sup>9</sup>

A trans pyramidal  $InN_2(CO_2)_2$  building unit has been produced from the reaction of the same starting materials in *N,N'*-dimethylformamide (DMF), EtOH, and 1,2-diaminocyclohexane (1,2-DACH), which gives rodlike crystals formulated as  $In_6(2,5-PDC)_{12}(1,2-H_2DACH)_2(DMF)_5(EtOH)_5(H_3O)_2$  (**2**) by elemental microanalysis and single-crystal X-ray diffraction studies.<sup>10,11</sup> The crystallographic analysis of **2** revealed that its structure is composed of discrete metal–organic octahedra,  $[In_6(2,5-PDC)_{12}]^{6-}$ . In the crystal structure of **2** (Figure 2), each anionic octahedron resides in position around the crystallographic center of symmetry and

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**Figure 2.** (a) Optical image of **2**. Crystal structure of **2**: (b) illustration of  $\text{InN}_2(\text{CO}_2)_4$  MBB, which can be viewed as a 4-connected node,  $\text{trans-InN}_2(\text{CO}_2)_2$ , (c) a view of the octahedron cage with one encapsulated ethanol molecule (space-filling model), (d) a schematic representation of the octahedron, (e) space-filling view through a corner, and (f) space-filling view along the trigonal windows (color scheme: carbon = gray, hydrogen = white, nitrogen = blue, oxygen = red, indium = green).

consists of six In(III) ions occupying the vertexes of the octahedron linked by 12 2,5-PDC ligands, forming the octahedron edges. Each In(III) ion is coordinated to two nitrogen and five oxygen atoms ( $\text{InN}_2(\text{CO}_2)_4$ ) from four 2,5-PDC ligands (Figure 2b). As in **1**, the In–N bonds and the In–(5-carboxylate) bonds direct the topology while the  $\alpha$ -carboxylates complete the metal ion coordination sphere, resulting in a 4-connected node,  $\text{InN}_2(\text{CO}_2)_2$ . Distortion from the ideal octahedron can be characterized by the maximal deviation from the average In–In distance value (8.378 Å) and from the In–In–In ideal angles of 60° and 90°: 0.192 Å (2.29%), 2.61° (4.35%), and 0.28° (0.31%), respectively (see Supporting Information). The isolated octahedron,  $[\text{In}_6(2,5\text{-PDC})_{12}]^{6-}$ , possesses an overall  $T_h$  symmetry.

Interesting structural features of compound **2** are its internal cavity and triangular windows. The cavity of the octahedron cluster encapsulates one EtOH molecule, which is statistically disordered around the center of symmetry. Six DMF and two EtOH molecules are partially situated in the eight triangular windows of the octahedron. The remaining EtOH and  $\text{H}_2\text{O}$  molecules are located in the interstices between the octahedra, as illustrated in Figure S3. The discrete octahedra are linked by *cis*-1,2- $\text{H}_2\text{DACH}$  via N–H··O hydrogen bonds to generate a 3-D network.

Although a mixture of isomers of 1,2-DACH can be used in the synthesis, only the *cis* isomer is found to direct the formation of **2**. Therefore, *cis*-1,2-DACH acts as a structure directing agent and, as a result, compound **2** offers potential for separation and recognition of the *cis* and *trans* isomers of 1,2-DACH. It should also be noted that crystal structures containing the *cis* isomer are rare.<sup>12</sup>

To the best of our knowledge, the  $[\text{In}_6(2,5\text{-PDC})_{12}]^{6-}$  polyhedron represents the first example of an  $\text{M}_6\text{L}_{12}$  metal–organic octahedron. A polynuclear  $\text{M}_6\text{M}_{12}$  complex,<sup>13</sup> and  $\text{M}_6\text{L}_4$ ,<sup>3a</sup> and  $\text{M}_6\text{L}_6$ <sup>14</sup> polyhedra have been reported; nevertheless, molecular octahedral assemblies are rare.

Here we have illustrated the utilization of single-metal-ion-based MBBs, via heterochelation and bridging, as a means toward the design and synthesis of metal–organic assemblies, both discrete and extended. Present work is in progress to broaden this approach to other multifunctional ligands containing simultaneously the chelating and bridging functionality, as well as to other molecular building blocks,  $\text{MX}_n\text{Y}_m$ .

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**Supporting Information Available:** XRPD and IR data, structure figures and X-ray crystallographic data (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558–1564. (b) Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13–28.
- (2) (a) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369–378. (b) Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705–714. (c) MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, *389*, 469–472. (d) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268–3292.
- (3) (a) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469–471. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (c) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983. (d) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330.
- (4) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554.
- (5) Liu, Y.; Kravtsov, V.; Walsh, R. D.; Poddar, P.; Srikanth, H.; Eddaoudi, M. *Chem. Commun.* **2004**, 2806–2807.
- (6) Preparation of **1**: 2,5- $\text{H}_2\text{PDC}$  (14.5 mg, 0.087 mmol),  $\text{In}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  (15.0 mg, 0.044 mmol), EtOH (1 mL),  $\text{H}_2\text{O}$  (1 mL), TMDP (0.1 mL, 0.95 M in DMF), and  $\text{HNO}_3$  (0.2 mL, 0.35 M in  $\text{H}_2\text{O}$ ) were added to a vial, and the solution was heated to 85 °C for 12 h. Colorless polyhedral crystals were collected and air-dried (17.6 mg, 62% yield). As-synthesized material is insoluble in  $\text{H}_2\text{O}$  and common organic solvents. Elemental analysis (%) for **1**,  $\text{C}_{27}\text{H}_{33}\text{N}_4\text{O}_8\text{In}$  calcd: C 49.36, H 5.03, N 8.53; found: C 48.67, H 4.93, N 8.71.
- (7) Crystallographic data of **1**:  $\text{C}_{27}\text{H}_{33}\text{InN}_4\text{O}_8$ ,  $M = 656.39$ , trigonal, space group  $R\bar{3}c$ ,  $a = b = 15.7870(19)$  Å,  $c = 51.509(13)$  Å,  $V = 11118(3)$  Å<sup>3</sup>,  $Z = 18$ . Final  $R$  indicates ( $I > 2\sigma(I)$ ):  $R_1 = 0.0651$ ,  $wR_2 = 0.1192$ .
- (8) (a) Moulton, B.; Lu, J.; Hajndl, R.; Hariharan, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2821–2824. (b) Atwood, J. L. *Nat. Mater.* **2002**, *1*, 91–92. (c) 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. (d) Perry, J. J.; McManus, G. J.; Zaworotko, M. J. *Chem. Commun.* **2004**, 2534–2535. (e) Shin, D. M.; Lee, I. S.; Chung, Y. K.; Lah, M. S. *Inorg. Chem.* **2003**, *42*, 5459–5461. (f) Rusanov, E. B.; Ponomarova, V. V.; Komarchuk, V. V.; Stoeckli-Evans, H.; Fernandez-Ibañez, E.; Stoeckli, F.; Sieler, J.; Domasevitch, K. V. *Angew. Chem., Int. Ed.* **2003**, *42*, 2499–2501.
- (9) (a) Behera, J. N.; Paul, G.; Choudhury, A.; Rao, C. N. R. *Chem. Commun.* **2004**, 456–457. (b) Grohol, D.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 2640–2646. (c) Greedan, J. E. *J. Mater. Chem.* **2001**, *11*, 37–53.
- (10) Preparation of **2**: 2,5- $\text{H}_2\text{PDC}$  (14.5 mg, 0.087 mmol),  $\text{In}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  (15.0 mg, 0.044 mmol), EtOH (1 mL), DMF (2 mL), 1,2-DACH (0.1 mL, 0.4 M in DMF), and  $\text{HNO}_3$  (0.25 mL, 0.35 M in DMF) were added to a vial, and the solution was heated to 85 °C for 12 h. Colorless rodlike crystals were collected and air-dried (18.6 mg, 73% yield). As-synthesized material is insoluble in  $\text{H}_2\text{O}$  and common organic solvents. Elemental analysis (%) for **2**,  $\text{C}_{121}\text{H}_{139}\text{N}_{21}\text{O}_{60}\text{In}_6$  calcd: C 41.06, H 3.96, N 8.32; found: C 41.89, H 3.67, N 8.54. **1** can also be synthesized using conditions similar to those for **2** with the only difference being the choice of the template.
- (11) Crystallographic data of **2**:  $\text{C}_{121}\text{H}_{139}\text{In}_6\text{N}_{21}\text{O}_{60}$ ,  $M = 3536.45$ , triclinic, space group  $P1$ ,  $a = 14.4111(13)$  Å,  $b = 16.0466(14)$  Å,  $c = 16.7388(15)$  Å,  $\alpha = 114.216(2)^\circ$ ,  $\beta = 95.441(2)^\circ$ ,  $\gamma = 91.595(2)^\circ$ ,  $V = 3504.8(5)$  Å<sup>3</sup>,  $Z = 1$ . Final  $R$  indicates ( $I > 2\sigma(I)$ ):  $R_1 = 0.0855$ ,  $wR_2 = 0.2155$ .
- (12) Of 197 crystal structures containing 1,2-DACH deposited in the Cambridge Structure Database (CSD), only 15 structures (7.6%) are based on *cis* configuration. Furthermore, all 19 crystal structures containing the diprotonated diamine, 1,2- $\text{H}_2\text{DACH}$ , are of *trans* geometry. Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31–37.
- (13) Chen, X. M.; Aubin, S. M. J.; Wu, Y. L.; Yang, Y. S.; Mak, T. C. W.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9600–9601.
- (14) (a) Hamilton, T. D.; Papaefstathiou, G. S.; MacGillivray, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 11606–11607. (b) Johnson, D. W.; Xu, J.; Saalfrank, R. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2882–2885.

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