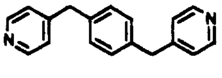
Interpenetrating Molecular Ladders and Bricks

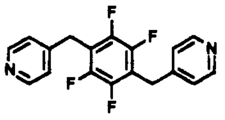
Makoto Fujita,*,† Yoon Jung Kwon,† Osamu Sasaki,†
Kentaro Yamaguchi,‡ and Katsuyuki Ogura*,†

Department of Applied Chemistry, Faculty of
Engineering, and Chemical Analysis Center
Chiba University, 1-33 Yayoicho
Inageku, Chiba 263, Japan

Received March 20, 1995

Interest in self-assembled infinite metal complexes with specific network topologies is expanding rapidly due to potential properties as functional solid materials.[1] Usually, the network topology can be designed by selecting the coordination geometry of metals and the chemical structure of organic ligands. In contrast to this understanding, we unprecedentedly observed the appearance of quite different network patterns from almost the same crystallographic molecules: i.e., upon complexation with $Cd(NO_3)_2$, pyridine-based ligand **1**[2] gave an infinite molecular ladder (pattern *a*) while ligand **2**,[3] a fluorinated analog of **1**, afforded an infinite molecular brick (pattern *b*), despite the very similar unit crystal structures of these complexes. We also found that the independent molecular ladders or bricks interpenetrate each other in their crystal structures.[4,5]

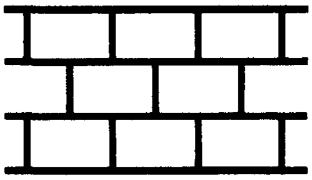

1



2

a

b



A single crystal of complex **3** having the empirical formula $[Cd(\mathbf{1})_{1.5}](NO_3)_2$ was obtained by allowing an ethanol−water (7:3) solution of **1** (75 mM) and $Cd(NO_3)_2$ (50 mM) to stand for 10 days at 20 °C and then subjected to an X-ray diffraction study. The yield of **3** amounted to 60%.

A crystallographic analysis[6] showed the existence of heptacoordinated geometry[7,8] on the Cd(II) atom and the T-shaped connection of three pyridyl groups in the molecular structure of **3** (Figure 1a). The geometry of the pyridyl groups around cadmium(II) is slightly deviated from an ideal T shape (N(1)−Cd(1)−N(2) = 85.5°, N(1)−Cd(1)−N(3) = 91.6 °, and N(2)−Cd(1)−N(3) = 176.1°). The more important feature is that infinite molecular ladders are formed in which the T-shaped units are linked to each other along the $a + b$ vector (Figure 2a).[10] These ladders involve very large 60-membered-ring structures in their backbones and are stacked on each other with an interplanar separation of 7.8 Å.

It is worth noting that another set of infinite ladders also exists along the $a - b$ vector, and the two sets of ladders, existing along the $a + b$ and $a - b$ vectors, interpenetrate each other as shown in Figure 2b. Because of this interpenetration, the ring involved in the ladder interlocks with four rings of different ladders.[11]

Essentially the same molecular structure was obtained for complex **4** prepared from **2** and $Cd(NO_3)_2$ (Figure 1b):[12] heptacoordination and the T-shaped connection[13] around cadmium(II) were again observed. Nevertheless, the infinite structure of **4** was quite different from that of **3**. The unit structure repeats along the $2a - c$ vector accompanying the alternative reversion of the geometry, making an unprecedented brick pattern (Figure 3a)[14] that involves a large, 90-membered-ring structure.

---

† Department of Applied Chemistry, Faculty of Engineering, Chiba University.

‡ Chemical Analysis Center, Chiba University.

(1) (a) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; Bein, T., Ed.; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992; Chapter 19. (b) Iwamoto, T. (Chapter 2); Liplowski, J. (Chapter 3); Hanotier, J.; Radzitzky, P. de (Chapter 4) *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol 1, Chapters 2−4, pp 29−134. (c) Iwamoto, T. *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1991; Vol 5, Chapter 6, pp 177−212.

(2) Physical properties of **1**: Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720.

(3) Physical properties of **2**: Fujita, M.; Nagao, S.; Iida, M.; Ogata, K.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574.

(4) For interpenetrating complexes composed of inorganic components with or without small organic ligands, see the following. (a) Soma, T.; Yuge, H.; Iwamoto, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1665. (b) Hoskins, B. F.; Robson, R.; Scarlett, N. V. Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2025. (c) Michaelides, A.; Kiritsis, V.; Skoulika, S.; Aubry, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1495. (d) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878. (e) Konnert, J.; Britton, D. *Inorg. Chem.* **1966**, *5*, 1193.

(5) For interpenetrating complexes containing large organic ligands, see the following. (a) Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1677. (b) Batten, S. R.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1991**, 445. (c) Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 8719. (d) Sinzger, K.; Hünig, S.; Jopp, M.; Bauer, D.; Bietsch, W.; von Schutz, J. U.; Wulf, H. C.; Kremer, R. K.; Metzenthin, T.; Bau, R.; Khan, S. I.; Lindbaum, A.; Lengauer, C. L. Tillmans, E. *J. Am. Chem. Soc.* **1993**, *115*, 7696. (e) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727. (f) MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325. (g) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755. (h) Real, J. A.; Andrés, E.; Muñoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265. (i) Rouzo, S.; Rabinowicz, M.; Briais, A. *Nature* **1995**, *374*, 795. (j) Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 574.

(6) Crystal data of **3**: monoclinic, $P2_1/n$; $a = 9.664(1)$ Å, $b = 13.427(2)$ Å, $c = 20.844(3)$ Å, $\beta = 94.74(1)°$; $V = 2695.5(6)$ Å^3; $Z = 4$; $d_{calc} = 1.55$ g cm^{-3}; $F(000) = 1268$; $\mu(\mathrm{Cu}\ K\alpha) = 69.12$ cm^{-1}; $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$ Å; temperature, −100 °C; 4410 reflections measured, 3447 observed ($F > 3.00\sigma(F)$); number of parameters 448; $R = 0.036$; $R_w = 0.044$. Anal. Calcd for $C_{27}H_{24}N_5O_6Cd$: C, 51.73; H, 3.86; N, 11.17. Found: C, 51.61; H, 3.81; N, 10.98.

(7) The heptacoordination geometry around the Cd cations: (a) Charles, N. G.; Griffith, E. A. H.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1983**, 22, 2717. (b) Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1608. (c) Fujita, M.; Kwon, Y. J.; Miyazawa, M.; Ogura, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1977.

(8) The distances of four Cd(II)−O bonds (2.40−2.56 Å) and three Cd(II)−N bonds (2.28−2.38 Å) are similar to those of normal $Cd(II)-ONO_2$ (2.49 Å) and Cd−N(pyridyl) bonds (2.36−2.37 Å), respectively,[9] featuring heptacoordination.

(9) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.

(10) An infinite ladder complex: Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Latour, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 11566.

(11) Though three interlocks, at most, are observed in Figure 2b, full symmetry operation gives four interlocks at each ring.

(12) An aqueous solution (0.25 mL) of $Cd(NO_3)_2$ (0.06 mmol) and an ethanol solution (1 mL) of **2** (0.09 mmol) were combined, and the solution was allowed to stand for 3 days at 20 °C to give colorless crystals of **4**: 63% yield; mp >300 °C; IR (KBr) 1612, 1482, 1378, 1288, 996 cm^{-1}. Crystal data of **4**: monoclinic, $P2_1/c$; $a = 10.694(1)$ Å, $b = 12.225(2)$ Å, $c = 21.600(3)$ Å, $\beta = 99.14(1)°$; $V = 2788.0(6)$ Å^3; $Z = 4$; $d_{calc} = 1.75$ g cm^{-3}; $F(000) = 1460$; $\mu(\mathrm{Cu}\ K\alpha) = 71.11$ cm^{-1}; $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$ Å; temperature, 23 °C; 4642 reflections measured, 3086 observed ($F > 3.00\sigma(F)$); number of parameters 478; $R = 0.041$; $R_w = 0.046$. Anal. Calcd for $C_{27}H_{18}F_6N_5O_6Cd$: C, 44.13; H, 2.47; N, 9.53. Found: C, 44.11; H, 2.25; N, 9.41. Crystals of **3** or **4** were obtained even if $Cd(NO_3)_2$ was treated with 2 equiv of **1** or **2**, respectively.

(13) Geometrical deviations in **4**: N(1)−Cd(1)−N(2) = 164.7°, N(1)−Cd(1)−N(3) = 102.4°, and N(2)−Cd(1)−N(3) = 92.3°.

0002-7863/95/1517-7287$09.00/0

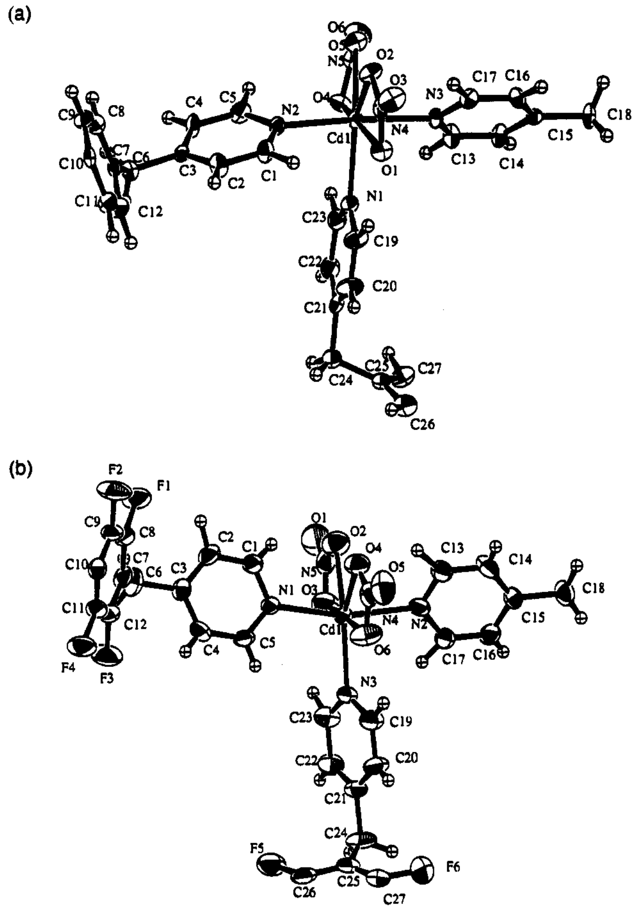


Figure 1. (a) Molecular structure of **3**. Selected bond distances (Å) and angles (deg): Cd(1)−O(1) 2.561(4), Cd(1)−O(2) 2.400(6), Cd(1)−O(4) 2.454(4), Cd(1)−O(5) 2.420(4), Cd(1)−N(1) 2.382(5), Cd(1)−N(2) 2.281(5), Cd(1)−N(3) 2.315(5), N(1)−Cd(1)−O(1) 84.1(2), N(1)−Cd(1)−O(4) 86.9(2), O(1)−Cd(1)−O(2) 52.4(1), O(2)−Cd(1)−O(5) 84.2(1), O(4)−Cd(1)−O(5) 52.7(1). (b) Molecular structure of **4**. Selected bond distances (Å) and angles (deg): Cd(1)−O(2) 2.446(6), Cd(1)−O(3) 2.412(6), Cd(1)−O(4) 2.459(6), Cd(1)−O(6) 2.433(6), Cd(1)−N(1) 2.316(6), Cd(1)−N(2) 2.325(6), Cd(1)−N(3) 2.335(6), N(3)−Cd(1)−O(3) 90.3(2), N(3)−Cd(1)−O(6) 84.1(6), O(2)−Cd(1)−O(3) 52.7(2), O(2)−Cd(1)−O(4) 80.8(6), O(4)−Cd(1)−O(6) 52.0(2).

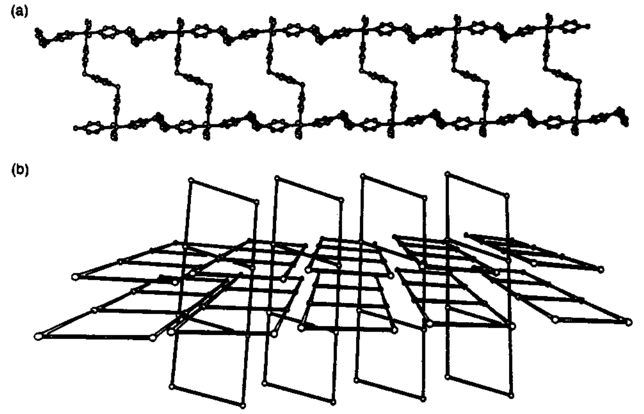


Figure 2. (a) Infinite ladder structure of **3**. (b) Perspective view of the frameworks in **3**. Only the Cd(II) centers are shown; heavy connections indicate Cd−**1**−Cd framework.

The whole crystal packing in **4** is significantly characterized by a triply interpenetrated two-dimensional sheet structure (Figure 3b). That is, three independent molecular bricks interpenetrate each other on the same plane, still making an infinite molecular sheet with a thickness of approximately 14 Å. The triple two-dimensional interpenetration could be distinguished from a few examples of the corresponding three-dimensional systems reported quite recently.[4a,b]

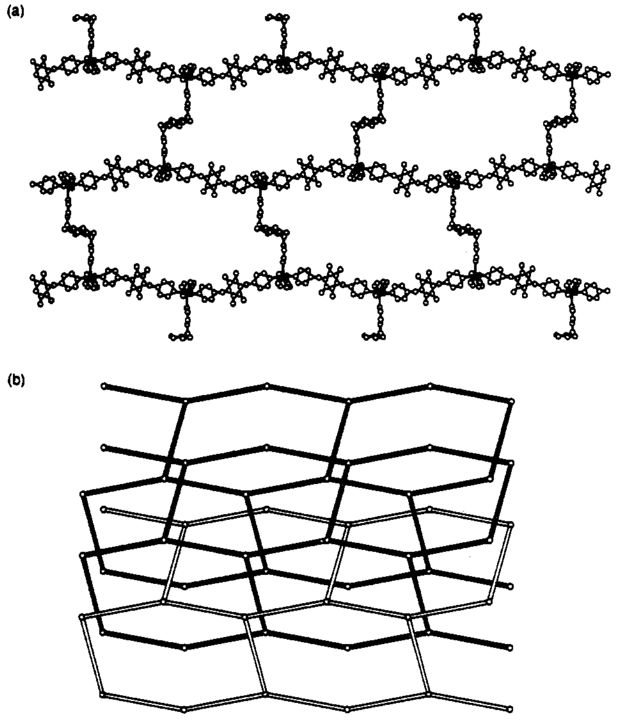


Figure 3. (a) Infinite brick structure of **4**. (b) Triply interpenetrated 2D sheet structure of **4**. Only the Cd(II) centers are shown; heavy connections indicate Cd−**2**−Cd framework.

It is interesting that infinite interlocking ring systems (polycatenane frameworks)[15] appear in both structures **3** and **4**, and this phenomenon nicely compliments the self-assembly of [2]-catenanes from transition metals (Pd(II) or Pt(II)) and ligand **1** or **2**.[2,16] Although the present study might emphasize the difficulty in designing the crystal structures of solid materials,[17] we are still seeking nice combinations of metals and organic ligands which afford fascinating finite or infinite frameworks according to or, more preferably, beyond our expectations.

Acknowledgment. This work was financially supported by the Ministry of Education, Science and Culture, Japan.

Supporting Information Available: Crystallographic data for **3** and **4** (57 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950912E

---

(14) The brick pattern can be regarded as a distorted honeycomb.[4e,5f]

(15) Polycatenane has become a challenging target. (a) Amabilino, D. B.; Ashton, P. R.; Reder, A. S.; Spencer, N.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 433. (b) Bitsch, F.; D.-Buchecker, C. O.; Khémiss, A.-K.; Sauvage, J. P.; Dorsselaer, A. V. *J. Am. Chem. Soc.* **1991**, *113*, 4023. (c) D.-Buchecker, C. O.; Frommberger, B.; Lüer, I.; Sauvage, J.-P.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.*, **1993**, *32*, 1434.

(16) Fujita, M.; Ibukuro, F.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 4175.

(17) (a) Desiraju, G. R. *Crystal Engineering: the Design of Organic Solids*; Elsevier: New York, 1989. (b) MacDonald, J. W.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383.