CHEMCOMM
Communication
www.rsc.org/chemcomm

Interpenetration in [Cd(isonicotinate)$_2$(1,2-bis(4-pyridyl)-ethane)$_{0.5}$(H$_2$O)]$_n$, a novel octahedral polymer containing an unusual two-dimensional bilayer motif generated by self-assembly of rectangle building blocks

Zhi-Yong Fu, Xin-Tao Wu,* Jing-Cao Dai, Li-Ming Wu, Chuan-Peng Cui and Sheng-Min Hu

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: wxt@ms.fjirsm.ac.cn

Received (in Cambridge, UK) 14th June 2001, Accepted 10th August 2001
First published as an Advance Article on the web 29th August 2001

A hydrothermally synthesized mixed-ligand molecular solid composed of pillared bilayers has been formulated; it presents a new remarkable three-dimensional architecture sustained by the catenation of two-fold decked layers, and exhibits intense photoluminescence upon photoexcitation at 314 nm.

In the realm of supramolecular chemistry, great interest has recently been focused on the crystal engineering of coordination frameworks due to their intriguing architectures, new topologies, intertwining phenomena and their potential application in microelectronics, nonlinear optics, molecular selection, ion exchange and catalysis.[1] Molecular self-assembly has emerged as an attractive approach to the fabrication of new materials;[2] this process involves the spontaneous aggregation of small molecular building blocks in solution that recognize each other through multiple molecular recognition sites to form extended architectures. What is particularly attractive is the novel types of structural motifs and supramolecular interdigitation observed in these species, exhibiting constituent motifs of dimensionality lower than that of the resulting overall architecture.[3] In the last decade, a wide range of polyrotaxanes and polycatenanes including those of honeycomb, brick wall, grid, T-shape, ladder, diamondoid and octahedral geometries, have been generated with simple, linear *N*,*N*'-donor spacers such as 4,4'-bipyridine, pyrazine and related species.[4] However, a novel structural motif known as a molecular bilayer had not been reported until recently,[5] and the crystal structure of double layer motifs are rare for coordination polymers.[6] Given the ubiquity of octahedral metal environments, simple octahedral polymers containing two-dimensional bilayer motifs remain largely unexplored. We report here on the preparation, crystal structure, thermal and luminescent properties of [Cd(isonicotinate)$_2$(1,2-bis(4-pyridyl)ethane)$_{0.5}$(H$_2$O]$_n$ **1**, a new member of this category of polycatenated motifs for octahedral polymers, which presents a new remarkable three-dimensional architecture sustained by the catenation of two-fold decked layers.

The hydrothermal reaction of Cd(NO$_3$)$_2$ with isonicotinic acid and 1,2-bis(4-pyridyl)ethane in molar ratio 2:2:1 at 115° C (1 day) led to the formation of colorless **1**. Elemental analysis confirmed the formula of **1**. X-Ray single-crystal analysis reveals that **1** contains two-dimensional bilayers with cuboids as the fundamental building units, in which each Cd^{II} center has a slightly distorted {CdN$_3$O$_3$} octahedral coordination sphere, with two nitrogen donors and two oxygen donors of four isonicotinate ligands in the equatorial plane. The coordination sphere is completed by one nitrogen donor of 1,2-bis(4-pyridyl)ethane and one oxygen donor of water (Fig. 1). Each cuboidal box consists of eight Cd^{II} atoms at the corners, connected by four long 1,2-bis(4-pyridyl)ethane and eight shorter isonicotinate linkers which make up the 12 edges.[7] This cuboidal structural motif is clearly different from those of tetrahedral building blocks to form other bilayer structures.[8]

Fig. 2(a) shows that the long ligands acting as pillars form bilayer galleries, in which planar sheets separated by them define 1D channels in the galleries (Fig. 2(b)). The channel width is established by the distance between cadmium atoms within a given planar sheet($d_{\mathrm{Cd-Cd}} \approx 9.697$ Å), and the height of the channel is established by the length of the pillar (14.025 Å). When viewed down along the crystallographic ***c*** axis, very regular square channels (crystallographic dimensions 9.697 × 9.697 Å) are evident in **1** (Fig. 2(c)). No guest molecules are encapsulated in these channels. A remarkable feature of **1** is that only one example of a coordination polymer with a 3D cuboidal framework has been reported[9] and no coordination polymers with cubiodal frameworks of two-dimensional bilayer motifs have been reported.

Although large channels exist in a single layer, they are mainly filled by other interpenetrated nets. Each one is interpenetrated by two adjacent (the upper and the lower ones) identical motifs. The resulting 3D array is, therefore, an infinite catenane of 2D architecture (Fig. 3), an intertwining type not observed previously in octahedral polymers.[10] The structure of **1** is in accord with the fact that crystal structures with such large cavities are stabilized either by inclusion of suitable guests or by interpenetrating lattices.

To study the stability of this material, thermogravimetric analysis (TGA) was performed on a polycrystalline sample (15.13 mg) of this material, which showed the following two strikingly clean and well-separated weight loss steps: an initial

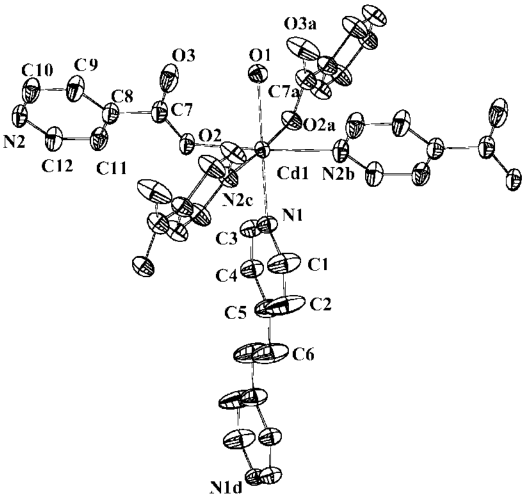

Fig. 1 ORTEP drawing of **1** around the Cd centre (ellipsoids at 50% probability); the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Cd(1)–O(2) 2.327(2), Cd(1)–O(2a) 2.327(2), Cd(1)–N(1) 2.351(4), Cd(1)–O(1) 2.365(3), Cd(1)–N(2b) 2.374(3), Cd(1)–N(2c) 2.374(3); O(2)–Cd(1)–O(2a) 90.94(12), O(1)–Cd(1)–N(2b) 86.08(9), N(2c)–Cd(1)–N(2b) 95.8(2), O(2)–Cd(1)–N(2c) 86.58(10), N(1)–Cd(1)–N(2c) 92.90(10), O(2)–Cd(1)–N(1) 89.23(9), O(2a)–Cd(1)–N(2b) 86.58(10), O(1)–Cd(1)–N(2c) 86.08(9), Symmetry codes: a = $x, -y, z$; b = $1/2 + x, 1/2 + y, z$; c = $1/2 + x, -1/2 - y, z$; d = $-1 - x, y, -2 - z$.

DOI: 10.1039/b105237n

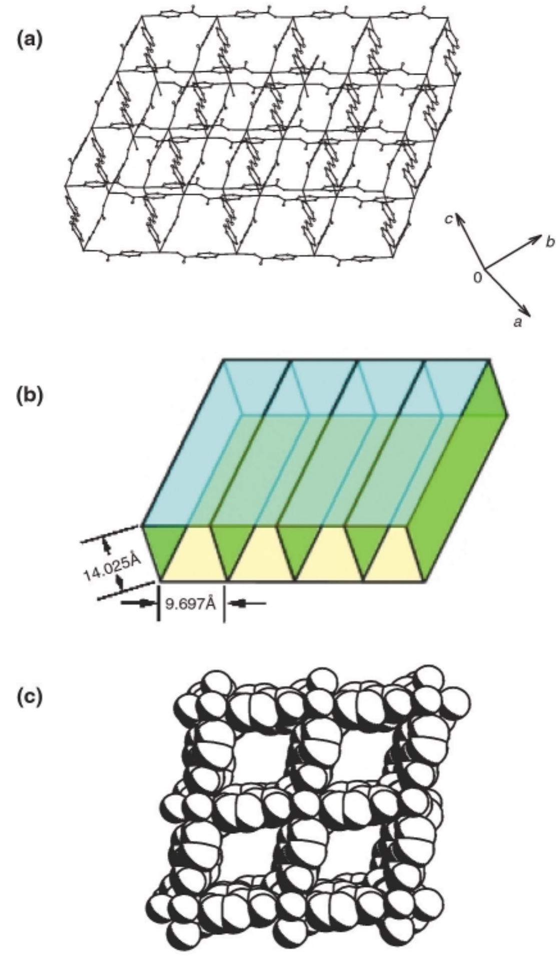

Fig. 2 (a) Pillared bilayer motif of **1**, (b) 1D channels in the bilayer galleries and (c) space filling model of the regular square cavity in the bilayer of **1**.

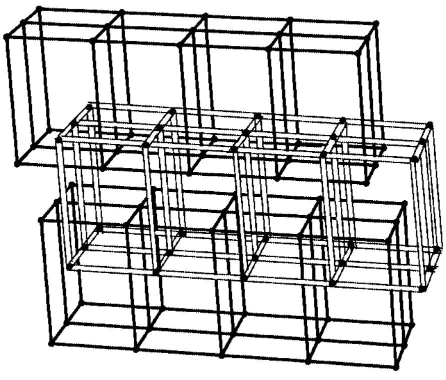

Fig. 3 The interpenetration model for complex **1**.

weight loss of 3.90% at 160 °C, corresponding to the removal of one water molecule per formula unit (calc. 3.85%), followed by another weight loss of 19.66% (calc. 19.73%) at 272 °C for evacuation of the pillars from the framework, with half a 1,2-bis(4-pyridyl)ethane molecule removed per formula unit. No further weight loss was observed until 412 °C.

In the solid state **1** exhibits intense photoluminescence upon photoexcitation at 314 nm,[11] which was measured with an Edinburgh F900 analytical instrument. The emission of **1** (λ_{max} = 509 nm) may be assigned as ligand-to-metal charge transfer (LMCT).[12] **1** may be a good candidate in blue-light emitting diode devices, since this condensed material is thermally stable and insoluble in common polar and non-polar solvents.

In conclusion, a novel octahedral polymer containing an unusual two-dimensional bilayer motif has been synthesized under hydrothermal conditions. This compound may be considered as a prototype of a potentially wide range of octahedral structures containing 2D bilayer motifs by using mixed bridging ligands. Further work on this subject is in progress.

This work is supported by grants from the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), the National Science Foundation (29733090, 29890210, 29873053) of China and the Science Foundation of Chinese Academy of Sciences.

Notes and references

† *Synthesis*: an aqueous mixture (10 cm^3) containing isonicotinic acid (1 mmol), Cd(NO$_3$)$_2$ (1 mmol), 1,2-bis(4-pyridyl)ethane (0.5 mmol) and NaOMe (1 mmol) was placed in a Parr Teflon-lined stainless steel vessel (25 cm^3), and the vessel was sealed and heated to 115 °C for 24 h, then cooled at 0.03 °C h^{-1} to room temperature. Colorless block-like crystals of **1** were obtained (0.16 g, 68.56%) (Anal. Calc. For $C_{18}H_{16}N_3O_5Cd$ **1**: C, 46.32; H, 3.46; N, 9.00. Found: C, 46.27; H, 3.072; N, 9.021%). IR (KBr pellet)/cm^{-1}: 3120w, 3064m, 2929m, 1614s, 1595s, 1552s, 1500w, 1439m, 1417s, 1385s, 1230m, 1063m, 1014m, 831s, 785s, 717m, 688s, 550w.

‡ *Crystal data* for compound **1**: $C_{18}H_{16}N_3O_5Cd$, M = 466.74, monoclinic, space group, $C2/m$, a = 12.6442(5), b = 14.7052(6), c = 11.1580(4) Å, β = 112.7730(10)°, U = 1912.94(13) Å^3, Z = 4, D_c = 1.621 Mg m^{-3}, F(000) = 932, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 1.175 mm^{-1}, 3472 reflections measured, 1717 unique (R_{int} = 0.0223), final $R1$ = 0.0302 for 1545 independent reflections [$I > 2\sigma(I)$]. The data collection was performed at room temperature on a Siemens SMART-CCD area-detector diffractometer. Data reductions and absorption corrections were performed with SMART and SADABS software, respectively. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXL93.[13] All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. CCDC reference number 165005. See http://www.rsc.org/suppdata/cc/b1/b105237n/ for crystallographic data in CIF or other electronic format.

1 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1461; M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, 283; P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; O. M. Yahi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; S. Noro, S. Kitagawa. M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2082.

2 J. M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995.

3 M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725; B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 1997, **119**, 2952.

4 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1461; K. N. Power, T. L. Hennigar and M. J. Zaworotko, *New. J. Chem.*, 1998, 177; S. Noro, S. Kitagawa. M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2082.

5 T. L. Hennigar, D. C. MacQuarrie, Pierre Losier, R. D. Roger and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972; K. N. Power, T. L. Hennigar and M. J. Zaworotko, *New. J. Chem.*, 1998, 177; L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio and S. Rizzato, *Chem. Eur. J.*, 1999, **5**, 237.

6 S. C. Zimmerman, *Science*, 1997, **276**, 543; V. A. Russel, C. C. Evans, W. Li and M. D. Ward, *Science*, 1997, **276**, 575.

7 To date, only a few molecular metal-based cubic compounds have been reported. These have been summarized recently: S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.

8 L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio and S. Rizzato, *Chem. Eur. J.*, 1999, **5**, 237; F. Q. Liu and T. D. Tilley, *Inorg. Chem.*, 1997, **36**, 5090.

9 Y. B. Dong, M. D. Smith and H. C. Loye, *Angew. Chem., Int. Ed.*, 2000, **39**, 4271.

10 To our knowledge, similar intertwining has been reported only in two examples of polymeric organic/inorganic compounds with tetrahedral coordination geometry: L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio and S. Rizzato, *Chem. Eur. J.*, 1999, **5**, 237; F. Q. Liu and T. D. Tilley, *Inorg. Chem.*, 1997, **36**, 5090.

11 d^{10} (Cu^{I}, Ag^{I}, Au^{I}, Zn^{II}, Cd^{II}) metal complexes have been found to exhibit intriguing structural and photoluminescent properties: P. D. Havey and H. B. Gray, *J. Am. Chem. Soc.*, 1988, **110**, 2145; K. R. Kyle, C. K. Ryu, J. A. DiBenedetto and P. C. Ford, *J. Am. Chem. Soc.*, 1991, **113**, 2954; P. C. Ford, E. Cariati and J. Bourassa, *Chem. Rev.*, 1999, **99**, 3625.

12 A. Meijerink, G. Blasse and M. Glasbeek, *J. Phys.: Condens. Matter.*, 1990, **2**, 6303; R. Bertoncello, M. Bettinelli, M. Cassrin, A. Gulino, E. Tondello and A. Vittadini, *Inorg. Chem.*, 1992, **31**, 1558.

13 G. M. Sheldrick, SHELXTL93: Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.