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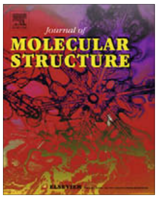

Formation of bilayer structure through face-to-face π–π interactions

Lei Jia [a,b], Ning Tang [a,*], Jagadese J. Vittal [c,*]

[a] College of Chemistry and Chemical Engineering and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China
[b] Currently at NUS on Student visit, National University of Singapore, Singapore 117543, Singapore
[c] Department of Chemistry, National University of Singapore, Singapore 117543, Singapore

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ABSTRACT

Self-assembly of $Cd(NO_3)_2{\cdot}4H_2O$ and *N*,*N*′,*N*″-tris(4-pyridinylmethyl)-1,3,5-benzene tricarboxamide (L) in DMF and further diffusion into ether furnished a new 2D coordination polymer, $[CdL_2(NO_3)_2]$. 2DMF (**1**) having noninterpenetrating honeycomb-like layer with (6,3) topology containing 54-membered rings and was characterized by elemental analyses, FT-IR, TGA and X-ray crystallography. These 2D sheets stack through face-to-face π–π interactions between central benzene rings and hydrogen bonding to form a bilayer structure. This type of perfect face-to-face π–π interactions (termed as Piedfort assemblies) are rare between benzene rings and its derivatives.

1. Introduction

During the past few years, design and synthesis of metal–organic frameworks have developed very rapidly, [1–3] because they may provide a new strategy for achieving functional solid materials with potential applications in molecular absorption, magnetism, ion exchange, electric conductivity and catalysis [4–5]. The use of covalent and noncovalent interactions to pack the molecular building blocks in a predictable manner has evolved into one of the most versatile strategies for the crystal engineering of extended networks [6–10]. The understanding and utilization of all noncovalent interactions, including π–π stacking, are essential for further development of inorganic supramolecular chemistry [11]. The solid-state structure of benzene has stimulated a great deal of interests due to the absence of the anticipated face-to-face π–π interactions [12]. Generally, π–π stacking interactions exist among the aromatic nitrogen-containing ligands in the metal complexes, but not between the benzene rings forming higher dimensional metal–organic coordination polymers. To the best of our knowledge, there are just only few examples containing the π–π interactions between 2D coordination polymeric sheets, [13–19] especially the extended structures by face-to-face interactions [14–17]. It may be realized that the perfect face-to-face π–π interactions involving benzene rings leading to two-dimensional polymers is a rare phenomenon.

The ligand *N*,*N*′,*N*″-tris(4-pyridinylmethyl)-1,3,5-benzene-tricarboxamide (L) which has a C_3-symmetric axis, had been used by Lah, Wei-Yin Sun and coworkers extensively to construct the nanocage structures with Cu(II) and Pd(II) ions recently [20–22]. When heptatopic Cd(II) ion is chosen instead of the hexatopic Cu(II) ion or tetratopic Pd(II) ion, the structure of the framework changed from nanocage to two-dimensional networks, and this happens to be the first layer structure formed by this type of ligand. Thus, we will describe the synthesis, and the 2D honeycomb structure of a novel MOF comprised of Cd(II) and a C_3-symmetric ligand L as a trigonal three-connection node, which is the first bilayer structure extended by noninterpenetrating 2D honeycomb-like layer via face-to-face π–π interaction stabilized by additional hydrogen bond interactions.

2. Experimental

2.1. General

All starting materials were obtained commercially and used as received. The elemental analyses were performed in the microanalytical laboratory, Department of Chemistry, National University of Singapore. The infrared spectra (KBr pellet) were recorded using an FTS165 Bio-Rad FT-IR spectrophotometer in the range of 4000–400 cm^{-1}. Solvent present in the crystals was determined using an SDT 2960 TGA thermal analyzer with a heating rate of 10 °C min^{-1} from room temperature to 600 °C.

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* Corresponding authors. Tel.: +65 6516 2975; fax: +65 6779 1691 (J.J. Vittal); Tel. +86 931 8911218 (N. Tang).
E-mail addresses: tangn@lzu.edu.cn (N. Tang), chmjjv@nus.edu.sg (J.J. Vittal).

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2.2. Sytheses of N,N′,N′′-tris(4-pyridinylmethyl)-1,3,5-benzenetricarboxamide (L) and the complex

Ligand L was synthesized according to a literature method [20]. The reaction of L (0.2 mmol, 0.1 g) with cadmium nitrate tetrahydrate (0.2 mmol, 0.064 g) in 3 ml of DMF solution at room temperature for 30 min gave a clear solution, the solution was filtered to a small tube and loaded into a large vial containing 15 ml of ether. The vial was sealed and left undisturbed at room temperature, which afforded colorless single needle-like crystals of the title compound within 10 days, with a ca. 67% yield (116 mg). FT-IR (KBr): ν_{NH} (3381), $\nu_{C=O}$ (1656) and ν_{NO3}(1454, 1290) cm^{-1}. Anal. Calc. (%) for dried compound $C_{27}H_{24}CdN_8O_9$: C 45.23, H 3.37, N 15.63; Found: C 45.12, H 3.56, N 15.60.

2.3. X-ray crystallography

Single-crystal X-ray diffraction measurements were made on a Bruker AXS SMART CCD diffractometer with Mo Kα (λ = 0.71073 Å) in a sealed tube. Unit cell dimensions were obtained with least-squares refinements, and all structures were solved by direct methods. The program SMART [23] was used to collect the intensity data, SAINT [23] for integration of the intensity, SADABS [24] for absorption correction and SHELXTL [25] for structure solution and refinements on F^2. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters assigned for all the non-hydrogen atoms. Selected crystallographic data is shown in Table 1 while selected bond lengths and angles are listed in Table 2, respectively. CCDC-690166 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via http://www.ccdc.can.ac.uk/conts/restrieving.hyml (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Table 1
Selected crystal data and structure refinement for compound **1**.

Formula	$C_{33}H_{38}CdNO_{11}$
Formula weight	863.13
Temperature	223(2) K
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	31.6334(16)
b (Å)	17.0235(7)
c (Å)	16.1104(7)
β (°)	112.809(2)
V (Å^3), Z	7997.2(6), 8
D_{calc} (g cm^{-3})	1.434
Absorption coefficient (mm^{-1})	0.614
F(000)	3536
Reflections collected	23311
Independent reflections	7043
R (int)	0.0444
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7043/21/516
Goodness-of-fit on F^2	1.023
Final R_1 and wR_2 [$I \geqslant 2\sigma(I)$]	0.0663, 0.2059
R_1 and wR_2 [all data]	0.0875, 0.2267
Largest diff. peak and hole (e Å^{-3})	1.413 and −0.488 e Å^{-3}

Table 2
Selected bond lengths [Å] and angles [°] for **1**.

Cd(1)—N(1)	2.298(5)	Cd(1)—O(2)	2.480(5)
Cd(1)—N(2)^a	2.297(5)	Cd(1)—O(4)	2.421(5)
Cd(1)—N(3)^b	2.329(5)	Cd(1)—O(5)	2.479(6)
Cd(1)—O(1)	2.437(5)		
N(2)^a—Cd(1)—N(1)	168.5(2)	N(1)—Cd(1)—O(5)	94.5(2)
N(2)^a—Cd(1)—N(3)^b	99.4(2)	N(3)^b—Cd(1)—O(5)	85.6(2)
N(1)—Cd(1)—N(3)^b	92.0(2)	O(4)—Cd(1)—O(5)	51.7(2)
N(2)^a—Cd(1)—O(4)	84.8(2)	O(1)—Cd(1)—O(5)	168.7(2)
N(1)—Cd(1)—O(4)	88.0(2)	N(2)^a—Cd(1)—O(2)	83.1(2)
N(3)^b—Cd(1)—O(4)	137.1(2)	N(1)—Cd(1)—O(2)	87.4(2)
N(2)^a—Cd(1)—O(1)	88.8(2)	N(3)^b—Cd(1)—O(2)	136.3(2)
N(1)—Cd(1)—O(1)	90.6(2)	O(4)—Cd(1)—O(2)	86.6(2)
N(3)^b—Cd(1)—O(1)	84.2(2)	O(1)—Cd(1)—O(2)	52.2(2)
O(4)—Cd(1)—O(1)	138.7(2)	O(5)—Cd(1)—O(2)	138.0(2)
N(2)^a—Cd(1)—O(5)	88.2(2)		

Symmetry transformations used to generate equivalent atoms.
[a] $x + 1/2, -y - 1/2, z + 1/2$.
[b] $x + 1/2, -y + 1/2, z + 1/2$.

3. Results and discussion

3.1. Structure description

Single-crystal X-ray diffraction studies reveal that **1** has a honeycomb-like open framework structure with (6,3) topology constructed from cadmium ions and the centroid of the benzene

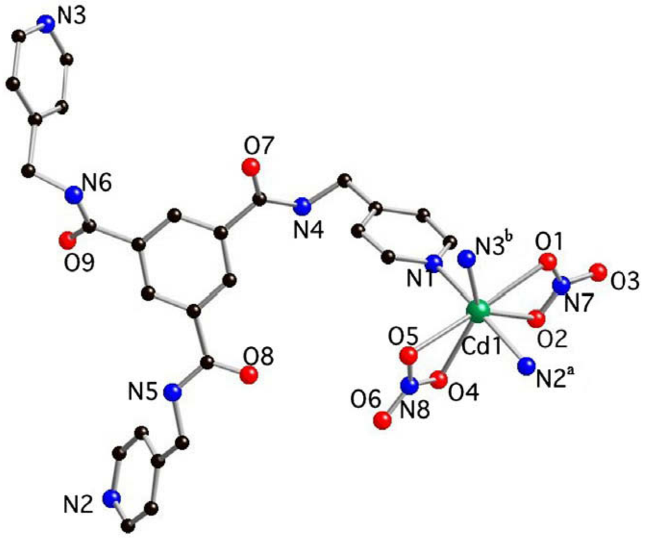

Fig. 1. The coordination environment of Cd(II) in **1**.

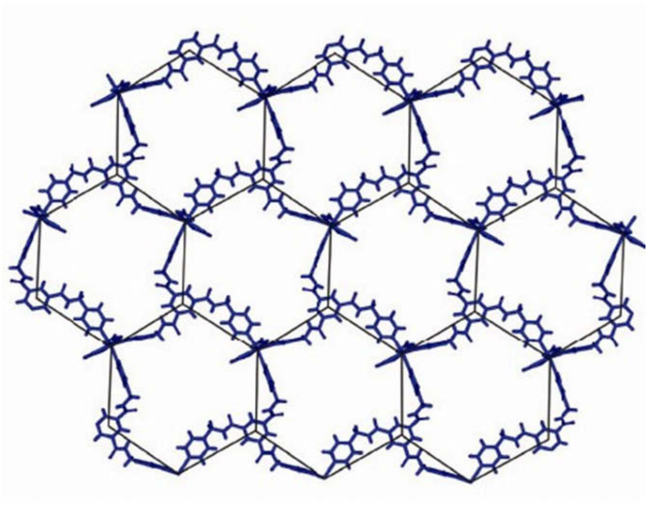

Fig. 2. The perspective view of the 2D layer with the honeycomb structure (dashed lines) in the *ab* plane of **1**.