LETTER

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A rare metal–organic 3D architecture with a pseudo-primitive cubic topology with double edges constructed from a 12-connected SBU†

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The hydrothermal assembly of $CdCl_2$ with isophthalatic acid (H_2ip) and 1,3-bis(4-pyridyl)propane (bpp) yielded a novel 3D coordination polymeric complex, $[Cd_4(ip)_4(bpp)_2]_n$ (1), which presents an interesting non-interpenetrated pseudo-primitive cubic (pcu) topology with double edges constructed from a 12-connected SBU.

Crystal engineering has provided chemists with a useful paradigm to develop rational approaches to design new solid-state materials based on the self-assembly of metal nodes with multifunctional ligands.[1] However, it is still a major challenge to control the assembly and 3D structure of the target compound.[2] Recently, Yaghi *et al.* have successfully developed a SBU (secondary building unit) strategy to direct the assembly of metal–organic frameworks (MOFs), which has been widely used for understanding and predicting structural topologies.[3] A large number of crystalline materials constructed from SBUs and links have been reported.[4] The most common SBUs are three-, four-, six-, or eight-connected nodes. Highly connected nodes remain very rare because the construction of such systems is severely hampered by the limited coordination sites of the metal and the steric nature of organic ligands. By combining the merits of polynuclear metal clusters and flexible ligands, we report herein a successful example of a novel non-interpenetrated pseudo-primitive cubic (pcu) topology with double edges constructed from a 12-connected SBU, namely $[Cd_4(ip)_4(bpp)_2]_n$ (**1**).

The effect of ligand flexibility on the structural properties of MOFs and the multiple coordination sites of cluster complexes inspired our research motivation. So a reaction system was designed based on the following considerations: (a) The use of carboxylate-bridged metal clusters as metal–organic SBUs to build extended self-assembly structures is relatively mature as we have already studied some benzoic multicarboxylate coordination polymers.[5] (b) The Cd(II) cation is a weak- to medium-strength acid able to coordinate simultaneously to both oxygen-containing hard bases and nitrogen-containing soft organic bases.[6] (c) The 1,3-bis(4-pyridyl)propane ligand, as a derivative of 4,4′-bipyridine is a flexible bidentate ligand owing to the three methylene groups between two 4-pyridyl rings.[5c,7]

The hydrothermal reaction of $CdCl_2$ with H_2ip, bpp and H_2O in a molar ratio 2 : 2 : 1 : 2000 at 160 °C led to the formation of the colorless air-stable complex **1**. The elemental analysis results match the formula of **1**. The IR spectrum shows the typical antisymmetric (1611 cm^{-1}) and symmetric (1558, 1448 and 1400 cm^{-1}) stretching bands of carboxylate groups in **1**. Their respective values of $[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)]$ clearly indicate the presence of chelating (53 cm^{-1}) and bridging (163 cm^{-1} and 211 cm^{-1}) coordination modes of the carboxylate groups in **1**. This structural information is consistent with the results of the X-ray analysis.

X-Ray single-crystal diffraction analysis reveals that the asymmetric unit of **1** contains two independent six-coordinated Cd(II) centers, namely Cd1 and Cd2. Both of them are bound to four carboxylate groups and one N donor of the bpp ligand. As shown in Fig. 1, two carboxylate groups inter-link $(Cd1)_2(Cd2)_2$ into a tetranuclear cluster unit (Cd1···Cd2 and Cd2···Cd2 distances are 3.566 Å and 3.857 Å, respectively), which is jointly coordinated by eight H_2ip and four bpp ligands. Looking into the structure of **1**, one finds there exist four types of coordination modes of the carboxylate groups of the ip ligand as illustrated in Scheme 1. In Fig. 1, four ip ligands act as μ_3-bridges, whose two carboxylate groups adopt mode A and mode B, respectively; the other four ip ligands act

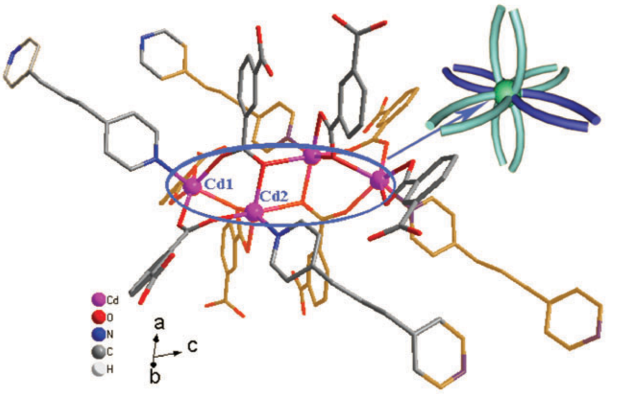

Fig. 1 Ball-and-stick representation of the tetranuclear Cd(II) cluster, showing a 12-connected SBU.

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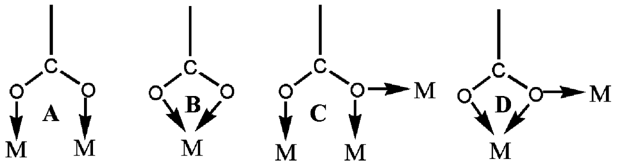
† Electronic supplementary information (ESI) available: Fig. S1: TGA curve of **1** and Fig. S2: emission spectra of **1**, H_2ip and bpp. See http://www.rsc.org/suppdata/nj/b5/b504917b/



Scheme 1 The four types of coordination modes of the carboxylate groups of ip ligands in **1**.

as μ$_5$-bridges, whose two carboxylate groups adopt mode C and mode D, respectively. The difference between Cd1 and Cd2 is that Cd1 is bound to four carboxylate groups in modes A, B, C and D; in contrast, Cd2 is bound to four carboxylate groups in modes A, C and D, but without mode B. Comparably, only two types of coordintion modes of the carboxylate groups of the ip ligand are found in $[Mn(ip)(bpp)_2] \cdot 0.5H_2O$ **2**,[8] which is also constructed by ip and bpp ligands, in chelating (mode B) and bismonodentate (mode A) modes, respectively.

If we take the tetranuclear Cd cluster as a single node located in the center of the cluster, this SBU becomes a 12-connected node. This is presently a rare example of a highly-connected SBU in coordination chemistry. Unfortunately, twelve links orient in six different directions and each pair of them chelates to another SBU. So each SBU only connects to six adjacent SBUs, making the whole structure a pseudo-pcu metal–organic architecture (Figs. 2 and 3).[9] There are two links between two nodes, so the architecture is very much similar to pcu with a double bond between two nodes (Scheme 2). Although the case of a 12-connected cluster unit that gives a 2-fold interpenetrated pcu net with double edges has been reported, such as $Zn_8(SiO_4)(tpht)_6$,[10] the present complex reveals different ligands and the first non-interpenetrated pcu net.

The tetranuclear Cd(II) clusters are bridged by ip ligands to form parallel square layers, $[Cd_4(ip)_4]_n$, of dimensions *ca.* 9.68 × 10.23 Å. The resulting layers are further pillared up by parallel bpp ligands to give the 3D structure $[Cd_4(ip)_4(bpp)_2]_n$ with the third dimension being about 16.88 Å (Figs. 2 and 3). This is in contrast to complex **2** in which the bpp ligand acts as a terminal ligand and the other N atom is left free.

The thermogravimetric analysis (TGA) of **1** was performed in an N_2 atmosphere when it was heated to 550 °C at a rate of 10 °C min^{-1}. The result shows that complex **1** is so stable that no obvious decomposition was observed below 370 °C. Complex **1** underwent a rapid and significant weight loss of 53.23% in the temperature range 370–440 °C, as shown in Fig. S1.† The remaining weight of 46.77% may correspond to the final product of $CdCO_3$ (calculated 45.90%).

The emission spectra of **1**, H_2ip and bpp in the solid-state at room temperature are shown in Fig. S2.† It can be observed that intense emissions occur at 422 nm and 517 nm (λ_{ex} = 310 nm) for **1**, 413 nm (λ_{ex} = 348 nm) for H_2ip, and 521nm (λ_{ex} = 400 nm) for bpp. To understand the nature of the two emission bands of **1**, we analyzed the photoluminescent properties of the H_2ip and bpp ligands and found that the two emission bands of **1** are in good agreement with those of H_2ip and bpp. Therefore, the two emissions may not be related to LMCT or MLCT. According to the literature,[11] they can be regarded as ligand-centered emissions jointly contributed to by these two ligands.

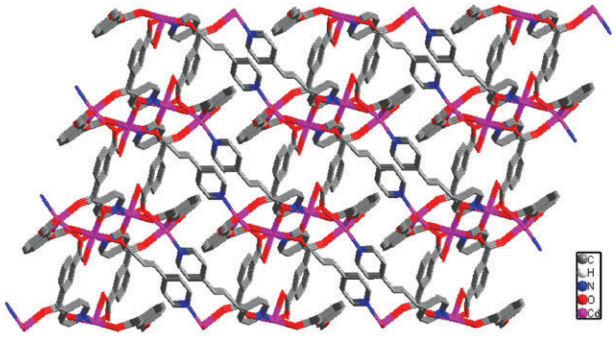


Fig. 2 The packing structure of complex **1**.

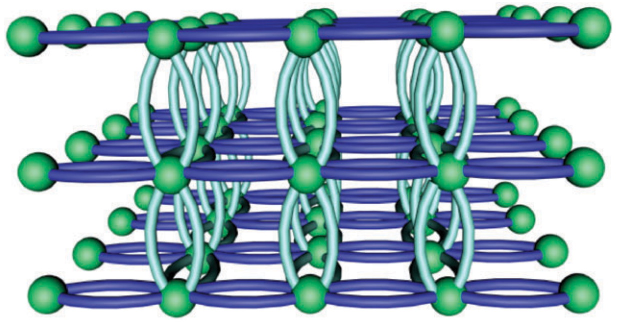


Fig. 3 Schematic representation of the 3D structure of complex **1** constructed from 12-connected SBUs. (ip ligand: jade-green line; bpp ligand: blue line)

In conclusion, by selecting a suitable synthetic strategy, we have successfully synthesized a novel Cd-MOF coordination polymer, which exhibits an interesting non-interpenetrated pseudo-pcu metal–organic 3D architecture constructed from a rare 12-connected SBU.

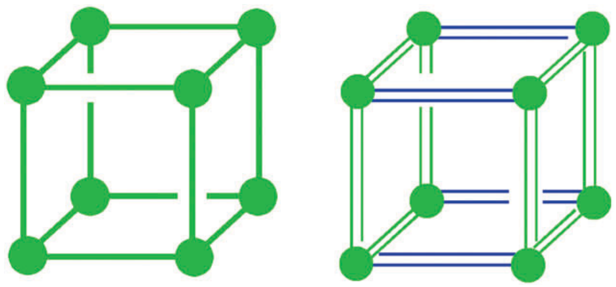
Experimental

Synthesis

The reactions were carried out by mixing $CdCl_2 \cdot 2.5H_2O$ (0.228 g, 1 mmol), H_2ip (0.166 g, 1 mmol), bpp (0.099 g, 0.5 mmol) and water (18 ml) in a 25 ml teflon-lined stainless-steel bomb. The reactor was heated to 433 K for 72 h and then was cooled slowly to room temperature (298 K) over a period of 3 days. The colorless prismatic single crystals of **1** were collected in about 42% yield. Anal. calcd. for $C_{58}H_{44}Cd_4N_4O_{16}$ (M = 1502.57) (%): C, 46.36; H, 2.95; N, 3.73. Found: C, 46.10; H, 2.69; N 3.99. IR (KBr, ν/cm^{-1}): 3436s, 3139s, 2926m, 2855m, 2170m, 1611s, 1558m, 1448s, 1400s, 1162m, 1019m, 806m, 759w, 742w, 713w, 613w, 515w.

X-Ray crystallography

A colorless crystal of **1** with dimensions 0.36 × 0.12 × 0.10 mm was mounted inside a glass fiber capillary. Data for complex **1** were measured with a Siemens Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298 K. Empirical absorption corrections were applied by use of the SADABS program.[12] The structures were solved by direct methods and all calculations were performed with the aid of the SHELXL PC program.[13] The structures were refined by full-matrix, least-squares minimization of $\sum(F_o - F_c)^2$ with anisotropic thermal parameters for all atoms except H atoms.



Scheme 2 Left: pcu net; right: the pseudo-pcu net with double edges.

Crystal data for 1‡. $C_{58}H_{44}Cd_4N_4O_{16}$, $M = 1502.57$, triclinic, space group $P\bar{1}$, $a = 9.67730(10)$, $b = 10.2288(2)$, $c = 14.8317(3)$ Å, $\alpha = 88.9600(10)$, $\beta = 71.7120(10)$, $\gamma = 75.7630(10)^\circ$, $V = 1348.40(4)$ Å^3, $Z = 1$, $Dc = 1.850$ g cm^{-3}, μ(Mo-Kα) = 1.633 mm^{-1}, $F(000) = 740$, $T = 293(2)$ K, 6889 reflections measured with 4631 unique reflections. The final $R = 0.0383$, w$R = 0.1006$ for 4154 observed reflections ($I > 2\sigma(I)$).

Acknowledgements

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‡ CCDC reference numbers 272567. See http://www.rsc.org/suppdata/nj/b5/b504917b/ for crystallographic data in CIF or other electronic format.