Organically templated metal–organic framework with 2-fold interpenetrated $\{3^3.5^9.6^3\}$-lcy net†

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Received (in Cambridge, UK) 3rd January 2008, Accepted 26th February 2008
First published as an Advance Article on the web 28th March 2008
DOI: 10.1039/b800017d

A new organic cation templated Zn(II) complex $(Et_3NH)[Zn_4(ip)_3(bta)_3]$ (1, ip = isophthalate, Hbta = benzotriazole) which consists of plate-like $Zn_4(bta)_3$ units bridged by ip ligands is reported; it is the first example of a 6-connected uninodal $\{3^3.5^9.6^3\}$-lcy net which has never been observed previously in MOFs but has been theoretically anticipated.

The recent progress in the synthesis of new crystalline microporous materials with novel compositional and topological characteristics promises new and advanced applications in shape or size selective adsorbents, ion exchangers, and catalysts.[1] One of the most important contributing factors for the diversity of crystalline microporous materials now known is the organic templating method. Especially, the use of positive-charged organic templates (also called structure-directing agents, most commonly tetraalkylammonium cations or protonated cationic amines) to direct the self-assembly of molecular precursors into extended frameworks is widely found in inorganic framework materials.[2,3] However, few 3-D covalent metal–organic frameworks (MOFs) with positive-charged organic templates are known.[4]

Here we report a new organic cation templated Zn(II) complex with unusual structural features. The compound $(Et_3NH)[Zn_4(ip)_3(bta)_3]$ (**1**, ip = isophthalate, Hbta = benzotriazole), exhibits an unusual 2-fold interpenetrating 6-connected host framework which consists of plate-like $Zn_4(bta)_3$ secondary building units (SBUs) bridged by ip ligands. The guest Et_3NH^+ cation lies on the plate-like $Zn_4(bta)_3$ unit and is further encapsulated by two single frameworks. To our knowledge, it is the first example of an unusual 6-connected $\{3^3.5^9.6^3\}$-lcy net which has never been observed previously in MOFs but has been theoretically anticipated. O'Keeffe *et al.* anticipated this net and stated "We do not know of an extended structure with a net based on lcy but the above discussion suggests that it would be an interesting challenge to attempt the design and synthesis of one."[5]

Colorless crystals of compound **1** were solvothermal synthesized by reacting $ZnSO_4 \cdot 7H_2O$ with Hbta and H_2ip in the presence of triethylamine at 160 °C.§ The structure of compound **1** was identified by satisfactory elemental analysis, IR and X-ray diffraction.¶

An unprecedented structural feature of **1** is the presence of the plate-like tetranuclear $Zn_4(bta)_3$ SBU. Fig. 1a shows this beautiful SBU containing four Zn atoms bridged by three bta ligands. The center Zn atom (Zn1) is located on a three-fold special position. The deprotonated bta ligand provides its three N donors to coordinate three Zn atoms, and the adjacent Zn1···Zn2 separation is 3.572 Å. Three edge-sharing 6-membered $[Zn_2N_4]$ metallacycles are formed, and the unit can be viewed as an extended aromatic system. Due to the different coordination geometries of Zn atoms (Zn1: octahedral geometry; Zn2: tetrahedral geometry), the atoms in the tetranuclear $Zn_4(bta)_3$ unit do not fall into one plane but form a plate-like structure. The bta ligand was widely used in the construction of metal–organic frameworks due to its multifunctional linking role,[6] and one discrete Cu(I) compound with a similar tetranuclear unit has been reported.[6d] To our knowledge, the tetranuclear $Zn_4(bta)_3$ unit presented here is the first example which acts as a SBU of an extended framework.

Each tetranuclear $Zn_4(bta)_3$ unit is bounded by six ip ligands and acts as a 6-connected node. Two carboxylate groups of the ip ligands adopt two different coordination modes: one bridges two independent Zn atoms and further stabilizes the tetranuclear $Zn_4(bta)_3$ unit, while another coordinates to Zn2 in monodentate fashion. Three ip ligands link three tetranuclear $Zn_4(bta)_3$ units to form a three-membered ring with an open window (Fig. 2a). The parallel stacking of the tetranuclear $Zn_4(bta)_3$ unit, the guest Et_3NH^+ cation and the three-membered ring results a sandwich-like structure (Fig. 1b). By reducing the tetranuclear $Zn_4(bta)_3$

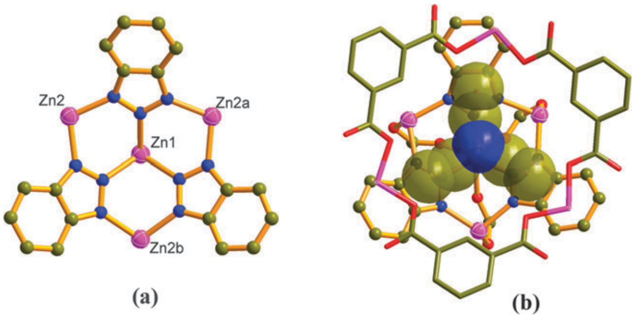

Fig. 1 (a) The plate-like tetranuclear $Zn_4(bta)_3$ SBU in **1**; (b) view of the sandwich-like structure, showing the encapsulation of the guest Et_3NH^+ cation (highlighted by space-filling mode).

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† Electronic supplementary information (ESI) available: Fig. S1–S4 showing 3D packing structure, photoluminescence spectra and TG-MS analysis; crystallographic data (CCDC 662784). See DOI: 10.1039/b800017d

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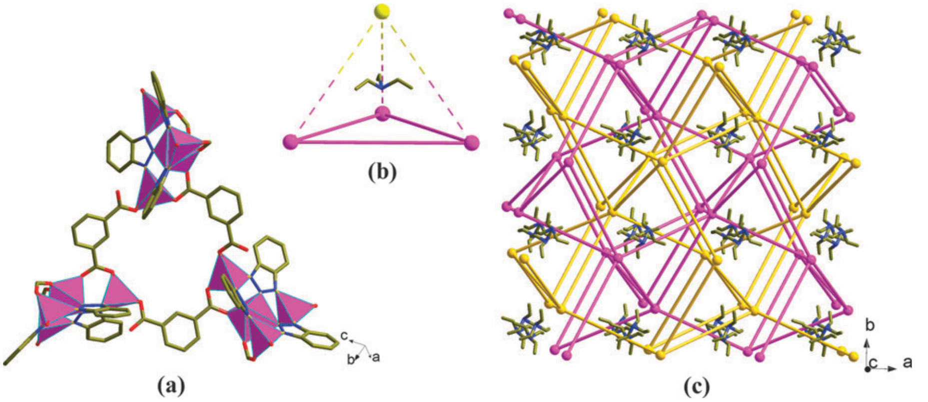

Fig. 2 (a) The 3-membered ring formed by three ip ligands bridging three tetranuclear $Zn_4(bta)_3$ SBUs; (b) schematic representation of the location of the guest Et_3NH^+ cation in a tetrahedron; (c) the 2-fold interpenetrated lcy network of **1** with the accommodation of the guest Et_3NH^+ cations.

unit to a single node, it is clear to illustrate that the guest Et_3NH^+ cation is located in the center of a tetrahedron (Fig. 2b).

The connectivity between the ip ligands and the tetranuclear $Zn_4(bta)_3$ units generates a 2-fold interpenetrating host framework (Fig. 2c). From the viewpoint of topology, it can be reduced to a 6-connected uninodal $\{3^3.5^9.6^3\}$ (denoted: lcy)[7] net by considering the tetranuclear $Zn_4(bta)_3$ unit as a 6-connected node and the ip ligand as a linker.[8,9] This net is obviously different from other known 6-connected topological nets.[10] The greatest difference from the lcy net to other common 6-connected nets (such as pcu, roa, rob, *etc.*) is the presence of the smallest 3-membered rings. For other 6-connected nets, they all are based on a (4,4) layered sub-structure and the smallest ring is a 4-membered ring.[10] Notably, the ideal lcy net has a chiral $P4_132$ space group and the maximum symmetry of the 2-fold interpenetrated net lcy presented here, however, is cubic $Pa\bar{3}$ due to the two subnets which are related by a center of symmetry. According to the typical classification of interpenetration, it can be assigned to class IIa.[11] Although the hetero-interpenetrating nets lcy + srs were observed in an inorganic compound Li_2Pt_3B previously,[12] to our knowledge the class IIa interpenetrating lcy nets observed in **1** are unprecedented.

The photoluminescent properties of compound **1** in the solid state at room temperature have also been studied. Upon excitation at 315 nm, **1** exhibits strong photoluminescence with emission maximum at 367 nm. According to the literature reports, Hbta ligand has a maximum emission at $\lambda_{em} = 350$ nm ($\lambda_{ex} = 300$ nm),[6e] H_2ip has a maximum emission at $\lambda_{em} = 408$ nm ($\lambda_{ex} = 348$ nm).[13] The emission spectrum of **1** is similar to that of the free Hbta ligand with a slight red shift, which indicates that the emission of **1** should be mostly derived from the π–π* transition of the bta ligand. TGA study shows that compound **1** is quite stable; no obvious decomposition was observed below 380 °C. A rapid and significant weight loss was observed between 380–910 °C, the remaining weight of 26.3% may correspond to the final product of ZnO (calculated 26.9%). Taking into account the combination of TG-MS, two observed species (*m*/*z*: 102 and 101) show strong flux signals in the MS spectrum when the decomposition reaction takes place. These two species can be assigned to $HNEt_3$ and NEt_3, respectively.

Despite the presence of the guest $HNEt_3$ ions, the solvent-accessible volume of the main framework is approximate 1712.1 Å^3 per unit cell volume and the pore volume ratio is calculated to be 15.2% using the PLATON program.[14] Heating–cooling experiments were carried out according to the TGA results and monitored by X-ray powder diffraction techniques (XPRD) (ESI Fig. S4†). Compared to the original crystals, the solid obtained by heating crystals of **1** to 350 °C shows an almost identical XPRD pattern. The result illustrates that the main framework of **1** is robust and maintains the porosity.

In conclusion, an interesting luminescent Zn compound with charged organic templates has been successfully obtained from solvothermal synthesis. It is the first example of an extended structure with a net based on lcy topology. The results reported here demonstrate that the organic templating method will enrich the area of crystalline microporous materials and host–guest chemistry.

This work was supported by the State Key Basic Research and Development Plan of China (2007CB815302), The Chinese Academy of Sciences (KJCX2-YW-M05), the NSF (E0620005) of Fujian Province, the Major Special Foundation of Fujian Province (2005HZ1027 and 2005HZ01-1), and the Fund of Fujian Key Laboratory of Nanomaterials (2006L2005).

Notes and references

§ A mixture of $ZnSO_4{\cdot}7H_2O$ (0.29 g, 1.0 mmol), Hbta (0.06 g, 0.5 mmol), H_2ip (0.08 g, 0.5 mmol) and triethylamine (0.1 g, 1.0 mmol) in molar ratio 2 : 1 : 1 : 2, together with 15 mL mixed MeOH–H_2O solvent (v/v = 1 : 2) were placed in a Parr Teflon-lined stainless steel vessel (25 cm^3), then the vessel was sealed and heated to 160 °C. The temperature was held for 3 days, then the reactant mixture was cooled slowly to room temperature, leading to the formation of red crystals of **1** (yield: 0.1019 g, 33% based on Zn). Anal. Calc. for **1**, $C_{48}H_{40}Zn_4O_{12}N_{10}$: C, 47.63; H, 3.45; N, 11.40%. Found: C, 47.15; H, 3.70; N, 11.60%. IR (solid KBr pellet, ν/cm^{-1}) for complex **1**: 3435 (s), 3138 (vs), 1625 (m), 1559 (w), 1400 (vs), 1164 (w), 747 (w).

¶ *Crystal data* for **1**: $C_{48}H_{40}Zn_4O_{12}N_{10}$, FW = 1210.43, cubic, $Pa\bar{3}$; $a = 22.4395(2)$, $b = 22.4395(2)$, $c = 22.4395(2)$ Å, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 90.00°$; $V = 11\,298.99(17)$ Å^3, $Z = 8$, $D_c = 1.423$ g cm^{-3},

$F(000) = 4912$, crystal size $= 0.50 \times 0.50 \times 0.40$ mm. The structure was solved by direct methods and refined by full matrix least-squares techniques. The final $R = 0.0410$, $wR2 = 0.1236$ and $S = 1.025$ for 4320 observed reflections with $I > 2.0\sigma(I)$. The ethyl groups of the $(Et_3NH)^+$ ion are slightly disordered and that as a consequence the ethyl H atoms were not included in the refinement. CCDC 662784. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b800017d

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