Two Zinc Architectures: A Mononuclear Complex and a 2D Wave-like Organic-inorganic Hybrid Layer①

JIN Mei-Fang DAI Fang-Na SUN Dao-Feng②

(Key Lab for Colloid and Interface Chemistry of Education Ministry, Department of Chemistry, Shandong University, Jinan 250100, China)

ABSTRACT Self-assembly of $Zn(NO_3)_2 \cdot 6H_2O$ and 2,3,5,6-tetrabromoterephthalic acid (**H_2TBTA**) gave rise to two new zinc metal-organic frameworks, $Zn(HTBTA)_2(phen)_2 \cdot H_2O$ (**1**) and $Zn(TBTA)_{1/2}(\mu_2\text{-}OH)(H_2O) \cdot 0.25EtOH$ (**2**). Complex **1** is a mononuclear molecule. The hydrogen bonding interactions further connect the mononuclear molecules to generate a 2D supramolecular architecture. Complex **2** is a 2D organic-inorganic hybrid layer framework constructed from 1D rod-shaped secondary building units.

Keywords: supramolecular architecture, zinc, metal-organic framework, mixed organic ligands, supramolecular interactions

1 INTRODUCTION

A lot of attention has been received in supramolecular chemistry and crystal engineering of metal-organic frameworks (MOFs) due to their potential power in the design and synthesis of functional materials with interesting structures, applications and desired topologies[1~3]. To explore these subjects in depth, the dexterous design and selection of organic ligand with desirable connectivity as well as the metal ions with appropriate coordination modes are crucial tasks[4, 5]. Among the numerous ligands, dicar-boxylic acid ligands such as 1,3-benzenedicarboxylic acid and terephthalic acid keeping versatile organic coordination modes have been widely employed in the construction of novel metal-organic fra- meworks with one-, two-, and three-dimensional fra- meworks[5~8]. To get new MOFs with various struc- tural types, much attention has been focused on selecting or synthesizing new ligands to construct porous MOFs which possess potential applications involving catalysis, separation and gas storage[9]. However, introducing uncoordinated functional groups bearing regulatory effects on the benzene rings has aroused less attention at this stage. Recently, we have applied 5-amino-2,4,6-triiodoisophthalic acid, a derivative of *m*-phthalic acid, as ligand to construct MOFs in which the iodine atoms act as the steric hindrance and the amino groups as hydrogen-bond donors, and a series of MOFs with interesting structural topologies has been synthesized[10~12]. What architecture will be generated if high steric hindrance groups are introduced into the terephthalic acid? Therefore, 2,3,5,6-tetrabromoterephthalic acid was selected in our work and it was found that the sizeable bromine atoms and contraposition of carboxylate groups make the H_2TBTA ligand incline to adopt straight line conformation to form low-dimensional architectures.

Besides, by introducing secondary organic ligands in the carboxylate systems, many metal-organic frameworks constructed from mixed organic ligands

Received 25 February 2010; accepted 27 May 2010 (CCDC 802459 and 802460)
① Supported by the NNSFC (20701025), the NSF of Shandong Province (Y2008B01), and Shandong University
② Corresponding author. Sun Dao-Feng, born in 1975, professor and doctor, majoring in coordination chemistry. E-mail: dfsun@sdu.edu.cn

have been designed and synthesized[13~16]. A common example of the mixed organic ligands is rich-carboxylate (aromatic acids or fatty acids) and N-containing (4,4′-bipyridine, 1,10-phenanthroline or their derivatives) ligands. Different from 4,4′-bipyridine and its derivatives, 1,10-phenanthroline and its derivatives have been used as a blocking ligand in the construction of low-dimensional frameworks due to their chelating coordination mode, which can prevent the framework from further extending[17~20]. Furthermore, their typical multi-aromatic ring and planar conformation feature them intermolecular interactions such as C–H···π, π···π and hydrogen-bonding interactions with other aromatic nucleus[21~24]. Some work has noticed the special "knock-on effect" of H_2TBTA[25, 26]. In this paper, we report the syntheses and crystal structures of two zinc MOFs: **1** and **2**, with a 2D supramolecular architecture based on mononuclear molecule through hydrogen bonding interactions, and a 2D wave-like organic-inorganic hybrid layer based on rod-shaped secondary building units. The roles of organic ligand and auxiliary coordinated chelating ligands, as well as the supramolecular interactions in these architectures, have also been discussed.

2 EXPERIMENTAL

2.1 Synthesis of 1

A methanol solution (5 mL) of $Zn(NO_3)_2·6H_2O$ (0.02 g, 0.06 mmol) was layered on 5 mL water solution containing H_2TBTA (0.01 g, 0.02 mmol) and phen (0.01 g, 0.05 mmol) in a tube. Colorless crystals of **1** suitable for X-ray analysis were obtained at the junction of the layer after a few days (yield: 65%).

2.2 Synthesis of 2

$Zn(NO_3)·6H_2O$ (0.02 g, 0.06 mmol) and H_2TBTA (0.01 g, 0.02 mmol) were dissolved in 4 mL EtOH and 4 mL H_2O at room temperature. The mixture in a 23-mL Parr Teflon-lined vessel was heated to 140 °C under autogenous pressure for 96 h, giving brown crystals in 85% yield (based on H_2TBTA).

2.3 Structure determination

Crystallographic data for **1** and **2** were collected on a Bruker Smart APEXII CCD diffractometer equipped with a graphite-monothematic Mo*Kα* radiation (λ = 0.71073 Å) at room temperature. Absorption corrections were applied using the multi-scan program SADABS[27]. Both structures were solved by direct methods using the SHELXS program of SHELXTL[28] package and refined by full-matrix least-squares techniques with SHELXL. The metal atoms in each complex were located from E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å).

3 RESULTS AND DISCUSSION

3.1 Crystal structure of complex 1

Single-crystal X-ray diffraction reveals that complex **1** crystallizes in monoclinic space group *C*2. The asymmetric unit of **1** consists of one zinc ion, one coordinated phen molecule, one $HTBTA^-$ ligand and one uncoordinated water molecule. As shown in Fig. 1, the central zinc ion is six-coordinated by two oxygen atoms from two coordinated $HTBTA^-$ ligands, four nitrogen atoms from two phen molecules with the average Zn–O and Zn–N distances of 2.109(7) and 2.156(5) Å, respectively.

The $HTBTA^-$ ligand is nonplanar due to the steric hindrance between the carboxylate groups and the bromine atoms, with the average dihedral angle between the carboxylate group and the central benzene ring of 118.2(4)°. One of the carboxylate groups of $HTBTA^-$ is deprotonated and coordinates to one zinc ion in a monodentate mode, while the other three oxygen atoms of $HTBTA^-$ are naked, which provide the hydrogen bonding donors or acceptors. The two phen liands are parallel to $HTBTA^-$, resulting in moderate intramolecular π···π interactions (3.6070 Å) (Fig. 1) to further stabilize the mononuclear molecule.

Fig. 2 shows strong O–H···O hydrogen bonds (O(1)–HO(1)···O(3), 2.604 Å) between protonated uncoordinated oxygen atoms and deprotonated uncoordinated oxygen atoms in the neighboring carboxylate groups of $HTBTA^-$, which connect discrete mononuclear molecules to form a 2D supramolecular architecture. Every mononuclear molecule attaches to four adjacent molecules through O–H···O hydrogen bonds. Thus, if the hydrogen bonds can be considered as the coordinative bonds and the zinc ion as the single node, the 2D supramolecular architecture of complex **1** is a (4,4) net, as shown in Fig. 3.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Complex 1		Complex 2	
Bond	Dist.	Bond	Dist.
Zn(1)–O(1)#2	2.107(4)	Zn(1)–O(4)	1.974(5)
Zn(1)–O(1)	2.107(4)	Zn(1)–O(4)#1	1.975(5)
Zn(1)–N(2)	2.123(4)	Zn(1)–O(2)	2.036(5)
Zn(1)–N(2)#2	2.123(4)	Zn(1)–O(3)	2.069(5)
Zn(1)–N(1)	2.191(4)	Zn(1)–O(1)	2.147(5)
Zn(1)–N(1)#2	2.191(4)		
Angle	(°)	Angle	(°)
O(1)#2–Zn(1)–O(1)	88.4(2)	O(4)–Zn(1)–O(4)#1	133.20(12)
O(1)#2–Zn(1)–N(2)	90.54(15)	O(4)–Zn(1)–O(2)	113.8(2)
O(1)–Zn(1)–N(2)	97.72(16)	O(4)#1–Zn(1)–O(2)	111.3(2)
O(1)#2–Zn(1)–N(2)#2	97.72(16)	O(4)–Zn(1)–O(3)	96.7(2)
O(1)–Zn(1)–N(2)#2	90.54(15)	O(4)#1–Zn(1)–O(3)	91.1(2)
N(2)–Zn(1)–N(2)#2	168.5(2)	O(2)–Zn(1)–O(3)	95.1(2)
O(1)#2–Zn(1)–N(1)	168.09(15	O(4)–Zn(1)–O(1)	88.0(2)
O(1)–Zn(1)–N(1)	94.24(14)	O(4)#1–Zn(1)–O(1)	87.1(2)
N(2)–Zn(1)–N(1)	77.60(15)	O(2)–Zn(1)–O(1)	81.3(2)
N(2)#2–Zn(1)–N(1)	93.87(16)	O(3)–Zn(1)–O(1)	175.0(2)
O(1)#2–Zn(1)–N(1)#2	94.24(14)		
O(1)–Zn(1)–N(1)#2	168.09(15		
N(2)–Zn(1)–N(1)#2	93.87(16)		
N(2)#2–Zn(1)–N(1)#2	77.60(15)		
N(1)–Zn(1)–N(1)#2	85.5(2)		

Symmetry operations: #2: $-x-1, y, -z-1$ for **1**; #1: $-x+1, y+1/2, -z+1/2$ for **2**

Table 2. Crystal Data for Complexes 1 and 2

Complex	1	2
Formula	$C_{40}H_{20}Br_8N_4O_9Zn$	$C_{4.5}H_{4.5}Br_2O_{4.25}Zn$
Formula weight	1405.19	351.77
Crystal size/mm	0.30 × 0.20 × 0.10	0.15 × 0.1 × 0.1
Crystal color	Colorless	Brown
Crystal system	Monoclinic	Orthorhombic
Space group	*C2*	*Pbca*
a/Å	16.155(6)	11.149(5)
b/Å	10.055(4)	6.199(3)
c/Å	14.183(6)	21.727(10)
α/deg	90.00	90.00
β/deg	113.533(6)	90.00
γ/deg	90.00	90.00
V/Å^3	2112.4(15)	1501.6(12)
Z	2	8

To be continued

D_c /g·cm^{-3}	2.209	2.983
F(000)	1340.0	1259.0
μ/mm^{-1}	8.209	13.872
Indpndt reflcns	4290	1814
GOF	0.925	0.932
R, wR ($I > 2\sigma(I)$)	0.0277, 0.0628	0.0516, 0.1151
R, wR (All data)	0.0353, 0.0660	0.0763, 0.1243

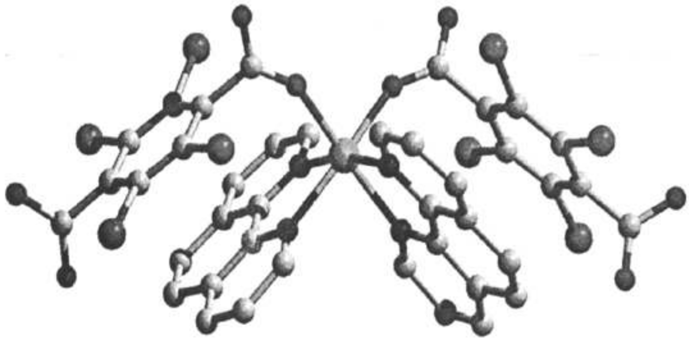

Fig. 1. Molecular structure of 1

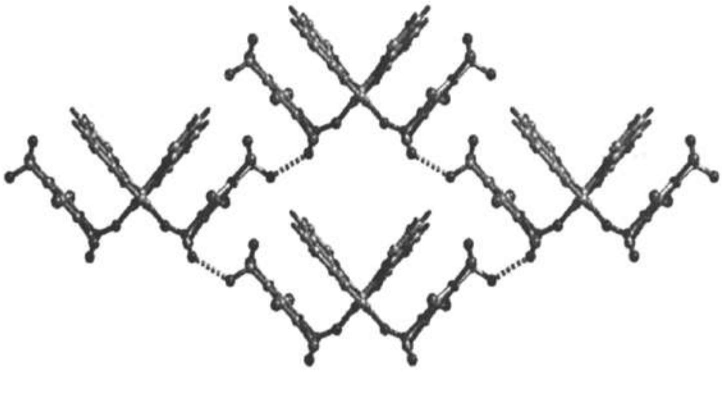

Fig. 2. Intermolecular O–H···O hydrogen bonds in 1

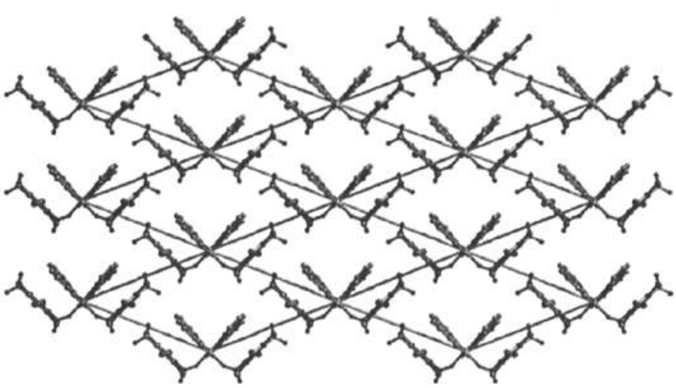

Fig. 3. 2D supramolecular architecture with (4,4) net

3. 2. Crystal structure of complex 2

Single-crystal X-ray diffraction reveals that complex **2** crystallizes in orthorhombic space group *Pbca*. The asymmetric unit of **2** contains one zinc ion, a half $TBTA^{2-}$ ligand and one coordinated water molecule. The central zinc ion is five-coordinated by two oxygen atoms from two $TBTA^{2-}$ ligands, two μ_2-OH groups and one coordinated water molecule in a trigonal bipyramidal geometry, with average bond length of 2.040(4) Å. Both carboxylate groups of TBTA are deprotonated and each adopts a bidentate bridging mode to link two zinc ions. Thus, the zinc ions are further connected by the μ_2-OH and carboxylate groups of TBTA to generate a one-dimensional inorganic chain (Fig. 4a), which is further linked by the bridging TBTA ligands to form a two-dimensional organic-inorganic hybrid layer, as depicted in Fig. 4b. The inorganic chain can be considered as the rod-shaped secondary building unit of the whole structure[29]. The SBU consists of infinite (-O–Zn-) rods (Fig. 4a) with carboxylate O atoms, completing the trigonal coordination around zinc to result in an infinite rod of ZnO_5 bipyramid sharing opposite corners (Fig. 4c). The carboxylate C atoms are at the vertices of a zigzag line SBU. Joining the inorganic SBU lines through organic -C_6Br_4- linkers lead to a two-dimensional organic-inorganic net work.

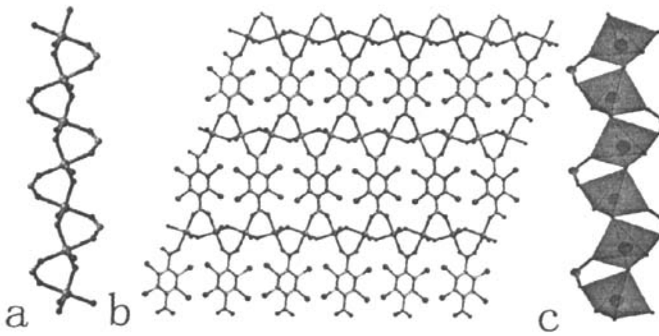

Fig. 4. a) Inorganic line of famous rod-shaped secondary building units, b) 2-D dimensional organic-inorganic hybrid network, c) ZnO_5 bipyramidal polyhedra in compound 2

The coordinated water molecules point out to the layer, providing hydrogen bonding donors. The strong hydrogen bonding interactions (O(2)–H(2)···O(4), 2.687 Å) between coordinated water molecules in one layer and μ_2-OH group in its adjacent layer (Fig. 5a) further connect **2** to yield a 3D supramolecular architecture (Fig. 5b). Thus, complex **2** can also be considered as a 3D organic-inorganic hybrid supramolecular architecture.

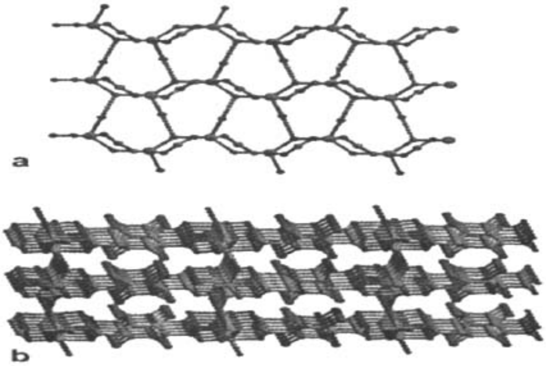

Fig. 5. a) Strong hydrogen bonding interactions between the coordinated water molecules and μ_2-OH group; b) 3D supramolecular architecture of 2

3.3 Thermogravimetric analysis

Thermogravimetric analysis has been measured for complexes 1 and 2. From Fig. 6, a TGA study on an as-isolated crystalline sample of **1** can be stable up to 210 ℃. The gradual weight loss of 1.2% from 50 to 198 ℃ corresponds to the release of one coordinated water molecule (calcd.: 1.3%); and above 210 ℃, **1** starts to decompose. For complex **2**, the first weight loss of 8.3% from 50 to 156 ℃ is due to the removal of coordinated water molecule (calcd.: 8.7%), and after that, **2** starts to decompose.

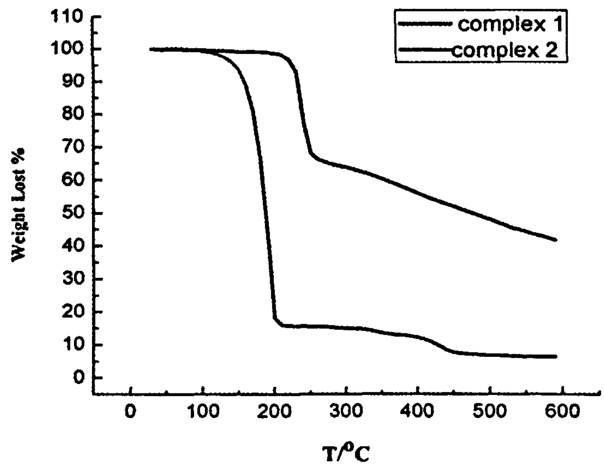

Fig. 6. Thermogravimetric analyses for complexes 1 and 2

4 CONCLUSION

In summary, two zinc supramolecular frameworks have been synthesized and characterized. Complex **1** is a mononuclear complex, and the blocking ligand of phen plays an important role in forming the 0D molecule of **1**. However, without chelating ligand, complex **2** is a 2D organic-inorganic hybrid layer based on rod-shaped secondary building units. All the intermolecular interactions like $\pi\cdots\pi$ interactions and O–H···O hydrogen bonding play important roles in constucting these architectures. Studies on this subject as well as constructing 3D porous metal-organic frameworks with these mixed organic ligands are currently underway in our lab.

REFERENCES

(1) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* 2001, 101, 1629–1658.

(2) Kitagawa, S.; Kitaura, R.; Noro, S. I. *Angew. Chem. Int. Ed.* 2004, 43, 2334–2375.

(3) Evans, O. R.; Lin, W. *Acc. Chem. Res.* 2002, 35, 511–522.

(4) Yaghi, O. M.; Keeffe, M. O'; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* 2003, 423, 705–714.

(5) Bourne, S. A.; Lu, J. J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* 2001, 40, 2111–2117.

(6) Vodak, D. T.; Braun, M. E.; Kim, J.; Eddaoudi, M.; Yaghi, O. M. *Chem. Commun.* 2001, 2534–2535.

(7) Spencer, E. C.; Howard, J. A. K.; McIntyre, G. J.; Rowsell, J. L. C.; Yaghi, O. M. *Chem. Commun.* 2006, 278–280.

(8) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; 'Keeffe, M. O.; Yaghi, O. M. *Science* 2002, 295, 469–472.

(9) Chae, H. K.; Siberio-Pe'rez, D. Y.; Kim, J.; Go, Y. B.; Eddaoudi, M.; Matzger, A. J.; 'Keeffe, M. O.; Yaghi, O. M. *Nature* 2004, 427, 23–527.

(10) Dai, F. N.; He, H. Y.; Zhao, X. L.; Ke, Y. X.; Zhang, G. Q.; Sun, D. F. *CrystEngComm.* 2009, 12, 337–340.

(11) Dai, F. N.; He, H. Y.; Sun, D. F. *Inorg. Chem.* 2009, 48, 613–4615.

(12) Dai, F. N.; He, H. Y.; Sun, D. F. *J. Am. Chem. Soc.* 2008, 130, 14064–14065.

(13) Wang, X. L.; Bi, Y. F.; Lin, H. Y.; Liu, G. C. *Cryst. Growth Des.* 2007, 7, 1086–1091.

(14) Pan, L.; Liu, H. M.; Kely, S. P.; Huang, X. Y.; Olson, D. H.; Li, J. *Chem. Commun.* **2003**, 854–855.

(15) Wang, X. L.; Qin, C.; Wang, E. B.; Li, Y. G.; Su, Z. M.; Xu, L.; Carlucci, L. *Angew. Chem. Int. Ed.* **2005**, 44, 5824–5827.

(16) Gomez-Lor, B.; Gutierrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruiz-Valero, C.; Snejko, C. *Chem. Mater.* **2005**, 17, 2568–2573.

(17) Mukhopadhyay, S.; Armstrong, W. H. *Am. J. Chem. Soc.* **2003**, 125, 13010–13011.

(18) Dimitrou, K.; Brown, A. D.; Folting, K.; Christou, G. *Inorg. Chem.* **1999**, 38, 1834–1841.

(19) Chen, X. M.; Liu, G. F. *Chem. Eur. J.* **2002**, 8, 4811–4817.

(20) Li, Y. G.; Hao, N.; Lu, Y.; Wang, E. B.; Kang, Z. H.; Hu, C. W. *Inorg. Chem.* **2003**, 42, 3119–3124.

(21) Zhang, L. Y.; Liu, G. F.; Zheng, S. L.; Ye, B. H.; Zhang, X. M.; Chen X. M. *Eur. J. Inorg. Chem.* **2003**, 2965–2971.

(22) Zhou, Y. F.; Zhao, Y. J.; Sun, D. F.; Weng, J. B.; Cao, R.; Hong, M. C. *Polyhedron* **2003**, 22, 1231–1235.

(23) Wang, X. L.; Qin, C.; Wang, E. B.; Su, Z. M.; Xu, L.; Batten, S. R. *Chem. Commun.* **2005**, 4789–4791.

(24) Sun, D. F.; Cao, R.; Liang, Y. C.; Shi, Q.; Su, W. P.; Hong, M. C. *J. Chem. Soc., Dalton Trans.* **2001**, 2335–2340.

(25) Li, C. P.; Tian, Y. L.; Guo, Y. M. *Polyhedron* **2009**, 28, 505–510.

(26) Li, C. P.; Tian, Y. L.; Guo, Y. M. *Inorganic Chemistry Communications* **2008**, 11, 1405–1408.

(27) Sheldrick, G. M. *SADABS 2.05*, University of Göttingen, Germany.

(28) *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison **2000**.

(29) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B. L.; 'Keeffe, M. O.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, 127, 1504–1518.