



## Synthesis, Crystal Structure of Two-Dimensional Porous Network $[\text{Zn}(\text{dmbdc})(\text{py})]\cdot\text{NMP}]_{2n}$ (py = Pyridine, NMP = N-Methyl-pyrrolidone, $\text{H}_2\text{dmbdc}$ = 2,5-Dimethylbenzenedicarboxylic Acid)

F.K. WANG<sup>1,\*</sup> and S.Y. YANG<sup>2</sup>

<sup>1</sup>College of Material and Chemical Engineering, Research Center for Solar Photovoltaic Material Development and Application, West An-hui University, Lu'an 237012, P.R. China

<sup>2</sup>Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P.R. China

\*Corresponding author: Fax: +86 564 3305696; Tel: +86 564 3305801; E-mail: wangfangkuo2491@126.com

Received: 24 January 2014;

Accepted: 21 April 2014;

Published online: 10 January 2015;

AJC-16637

A 2D porous coordination polymer with (4,4) network  $[\text{Zn}(\text{dmbdc})(\text{py})]\cdot\text{NMP}]_{2n}$  **1**, ( $\text{H}_2\text{dmbdc}$  = 2,5-dimethylbenzenedicarboxylic acid, py = pyridine, NMP = N-methyl-pyrrolidone) crystallized in the triclinic, space group P-1,  $a = 9.9876(15)$ ,  $b = 10.975(7)$ ,  $c = 20.032(5)$  Å,  $\alpha = 77.23(3)$ ,  $\beta = 86.565(15)$ ,  $\gamma = 67.90(3)^\circ$ ,  $Z = 2$  and consists of paddle-wheel dinucleus Zinc SBUs coordinated with ancillary ligands pyridine in the two sides of (4,4) net. In the structure of **1**, the paddle-wheel SBUs was connected with adjacent four SBUs through four dmbdc in the plane to form 2D sheet along a axis and two guest molecules NMP accommodated in the holes of 2D networks.

**Keywords:** Porous Network, Paddle-wheel SBUs, Crystal structure.

### INTRODUCTION

Metal-organic coordination polymers have also been attracting great interest owing to their potential applications on the catalysis, sensor, electrochemical *etc.*<sup>1-3</sup>. The topology and properties of coordination polymers contain aromatic carboxylic acid received extensively attention from material scientists and chemists<sup>4,5</sup>. There are abundant diversity of coordination modes in carboxylic ligands, lead to number of frameworks were synthesized by carboxylic acid and metal ions for construct intriguing and useful coordination polymers<sup>6,7</sup>. Consider the process of assemble in the coordination polymers, besides react condition such as temperature, solvents, pH, reactant concentration and metal ions<sup>8-11</sup>, the influence of substitutes and ancillary ligands on the coordination polymers have been extensively reported<sup>12-14</sup>. In order to form the steady framework, the ligands contain different geometry will bear different space tropism when they coordinated to the metal ions and result in diverse structures. The variety of substitute groups could change the coordinated mode of metal ion and bring obvious diversity in the crystal structure of products, for instance,  $\text{CH}_3$ - and  $-\text{NO}_2$  in the ligands commonly can't coordinate with metal ion while  $-\text{NH}_2$  could coordinated with metal ion<sup>15</sup> such as  $\text{Mn}^{2+}$ . Increasing the space tropism of substitute in the group will enhance obstructive effect and the torsion of ligand will increase when coordinate with metal ion and the congregation of metal ions also decreasing accordingly.

Herein we report a novel 2D (3,4) porous framework structure  $[\text{Zn}(\text{dmbdc})(\text{py})]\cdot\text{NMP}]_{2n}$  **1**, contain paddle-wheel SBUs ( $\text{H}_2\text{dmbdc}$  = 2,5-dimethylbenzenedicarboxylic acid, py = pyridine, NMP = N-methyl-pyrrolidone).

### EXPERIMENTAL

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR performed on Nicolet 740 FTIR Spectrophotometer, the range of  $\lambda$  is 4000-400  $\text{cm}^{-1}$ , the sample platelet with KBr. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with  $\text{CuK}\alpha$  radiation.

**Synthesis:**  $[\text{Zn}(\text{dmbdc})(\text{py})]\cdot\text{NMP}]_{2n}$  **1**,  $\text{H}_2\text{dmbdc}$  (0.194 g, 1 mmol) and  $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (0.298 g, 1 mmol) were dissolved in NMP (8 mL), then pyridine (0.5 mL) was slowly added to the solution. The mixture was placed in a 25 mL conical flask, heated to 90 °C at the rate of 0.5 °C/min and kept at 90 °C for 3 days, then slowly cool down to room temperature at the rate of 0.2 °C/min. Colourless block crystals (0.144 g, yield 33.04 %) suitable for X-ray diffraction was separated by filtration, washed with deionized water and dried in air. Elemental Analysis  $[\text{ZnC}_{20}\text{H}_{20}\text{N}_2\text{O}_5]_{2n}$ : found (calc.) C 54.86 (55.12), H 4.43 (4.64), N 6.31 (6.43) %. FTIR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3448 (m), 2958 (w), 2925 (w), 2344 (w), 1943 (w), 1671 (m), 1633

(m), 1489 (w), 1451 (w), 1404 (s), 1350 (m), 1295 (w), 1220 (m), 1190 (m), 1150 (m), 1075 (m), 1046 (s), 912 (w), 846 (m), 793 (s), 758 (s), 699 (vs), 642 (w), 539 (m), 471 (m).

**X-ray crystallography:** Data collection for **1** were performed on a Bruker SMART Apex CCD diffractometer at 173 K with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Absorption correction was applied by using the multi-scan program SADABS<sup>16</sup>. The structure was solved by direct methods and non-hydrogen atoms were refined anisotropically by least-squares on F<sup>2</sup> using the SHELXTL program<sup>17</sup>. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table-1 and selected bond lengths and angles for **1** show in Table-2.

TABLE-1  
CRYSTALLOGRAPHIC DATA AND STRUCTURE  
REFINEMENT PARAMETERS FOR **1**

Empirical formula	Zn <sub>2</sub> C <sub>40</sub> H <sub>44</sub> N <sub>4</sub> O <sub>10</sub>
Formula weight	871.53
Crystal size (mm)	0.40 × 0.30 × 0.20
Crystal system	Triclinic
Space group	P-1
a (Å)	9.9876(15)
b (Å)	10.975(7)
c (Å)	20.032(5)
$\alpha$ (°)	77.23(3)
$\beta$ (°)	86.565(15)
$\gamma$ (°)	67.90(3)
V (Å <sup>3</sup> )	1983.4(13)
T (K)	173(2)
Z, D <sub>calcd</sub> (Mg/m <sup>3</sup> )	2, 1.459
F(000)	904
$\mu$ (mm <sup>-1</sup> )	2.010
$h_{\min}/h_{\max}$	-10/11
$k_{\min}/k_{\max}$	-12/11
$l_{\min}/l_{\max}$	-22/22
Ref. collected/ unique	14228/5920
R <sub>int</sub>	0.0271
Parameters	511
Max./min. transmissions	0.6892 / 0.5002
Final R indices [I > 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0402, wR <sub>2</sub> = 0.1284
R indices (all data)	R <sub>1</sub> = 0.0546, wR <sub>2</sub> = 0.1383
Goodness-of-fit on F <sup>2</sup>	1.130
Max./min., $\Delta\rho$ (e·Å <sup>-3</sup> )	0.994 / -0.665
Completeness (%)	97.4
$R_1 = \sum   F_o  -  F_c   / \sum  F_o $ , $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^{1/2}$	

## RESULTS AND DISCUSSION

**{[Zn(dmbdc)(py)]·NMP}<sub>2n</sub> (1):** Compound **1** was synthesized as brown block crystals by the reaction of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and H<sub>2</sub>dmbdc through hot solution method. The zinc ions lie in slightly distorted square-pyramidal coordination environment, coordinated by four oxygen atoms from four  $\mu_2$ -carboxylates and one oxygen atom from an ancillary ligand pyridine at the apex. Every two zinc ions are bridged by four carboxylates to form a common paddle-wheel SBU (Fig. 1), two pyridine lie in the two apex of SBU and the SBUs further connected with adjacent four SBUs by dmbdc ligands in the basal plane to form (4, 4) porous square networks along a axis (Fig. 2). The 2D net stacked by ABC mode along the c axis of the crystal structure (Fig. 3), the two ancillary ligand pyridine approach to the methyl of dmbdc in upper or down and the two ring of pyridine perpendicular to the adjacent layer of 2D networks. Each quadrangular void in the (4, 4) net accommodates two NMP from the adjacent layers above and below.

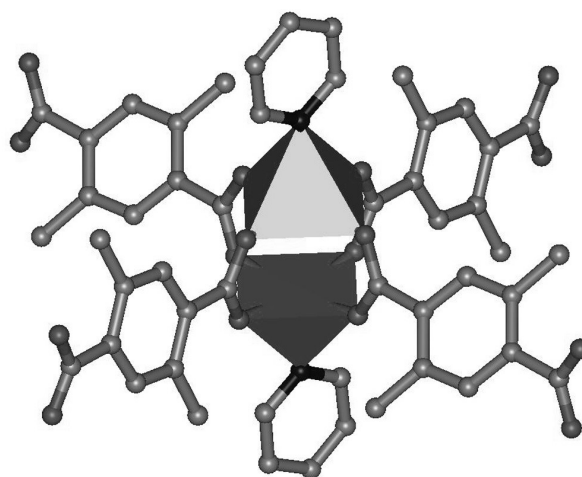


Fig. 1. Paddle-wheel dinuclear zinc SBUs of **1**. Hydrogen atoms are omitted for clarity

In X-ray powder diffraction pattern (Fig. 4), all of peaks among simulated curve are almost consistent with experimental data and the experimental value on the whole coincides with the calculation for elemental analysis measurement. Both they are shown that the pure phase of **1** was obtained through hot solution method in NMP. The most significant feature in the

TABLE-2  
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR **1**

Zn1-O2 <sup>i</sup>	2.0174(19)	O8-Zn2 <sup>ii</sup>	2.049(2)	O7-Zn2-O8 <sup>ii</sup>	159.89(10)
Zn1-O6 <sup>i</sup>	2.037(2)	Zn1-N1	2.036(3)	O2 <sup>i</sup> -Zn1-O6 <sup>i</sup>	88.57(10)
Zn1-O5	2.049(2)	Zn1-O1	2.040(2)	O2 <sup>i</sup> -Zn1-O1	159.83(9)
Zn2-O3	2.0145(19)	O2 <sup>i</sup> -Zn1-N1	101.85(9)	O6 <sup>i</sup> -Zn1-O1	87.91(10)
Zn2-O7	2.037(2)	N1-Zn1-O6 <sup>i</sup>	100.67(10)	N1-Zn1-O5	99.34(11)
Zn2-O8 <sup>ii</sup>	2.049(2)	N1-Zn1-O1	98.31(9)	O1-Zn1-O5	87.81(10)
O2-Zn1 <sup>i</sup>	2.0174(19)	O2 <sup>i</sup> -Zn1-O5	88.73(10)	O3-Zn2-O7	88.71(10)
O6-Zn1 <sup>i</sup>	2.037(2)	O6 <sup>i</sup> -Zn1-O5	159.94(10)	O3-Zn2-N2	101.39(9)
Zn1-Zn1 <sup>i</sup>	2.9372(11)	O3-Zn2-O4 <sup>ii</sup>	159.41(9)	O7-Zn2-N2	101.12(10)
Zn2-O4 <sup>ii</sup>	2.032(2)	O4 <sup>ii</sup> -Zn2-O7	87.65(10)	O4 <sup>ii</sup> -Zn2-O8 <sup>ii</sup>	88.40(10)
Zn2-N2	2.041(2)	O4 <sup>ii</sup> -Zn2-N2	99.20(9)	N2-Zn2-O8 <sup>ii</sup>	98.97(10)
O4-Zn2 <sup>ii</sup>	2.032(2)	O3-Zn2-O8 <sup>ii</sup>	88.08(10)	-	-

Symmetry codes: <sup>i</sup> -x + 1, -y + 1, -z + 1; <sup>ii</sup> -x + 2, -y + 1, -z

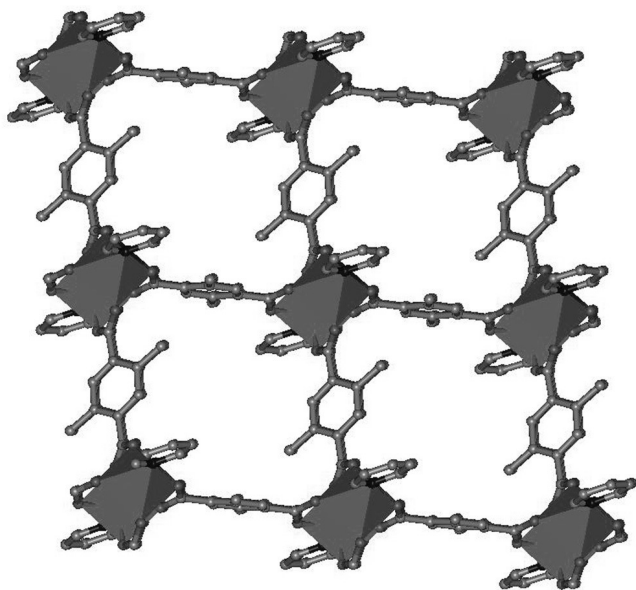


Fig. 2. View of the porous square (4, 4) net in **1** along a axis. Hydrogen atoms and guest molecules NMP are omitted for clarity

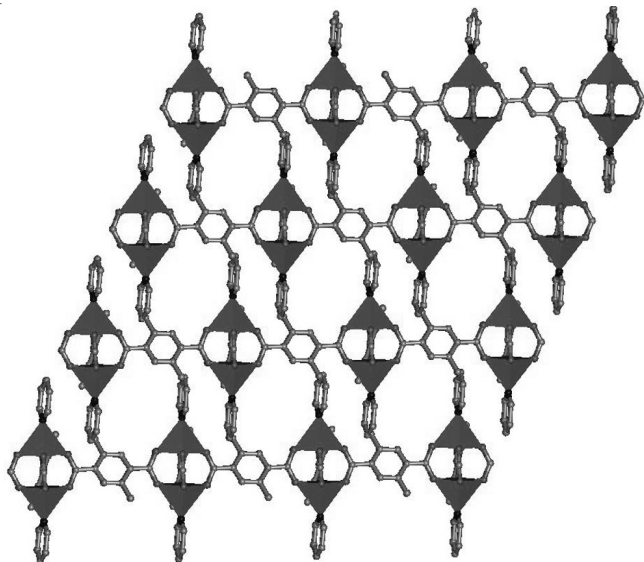


Fig. 3. A perspective view of the 2D sheets stacked by ABC mode in **1** along c axis. Hydrogen atoms and guest molecules NMP are omitted for clarity

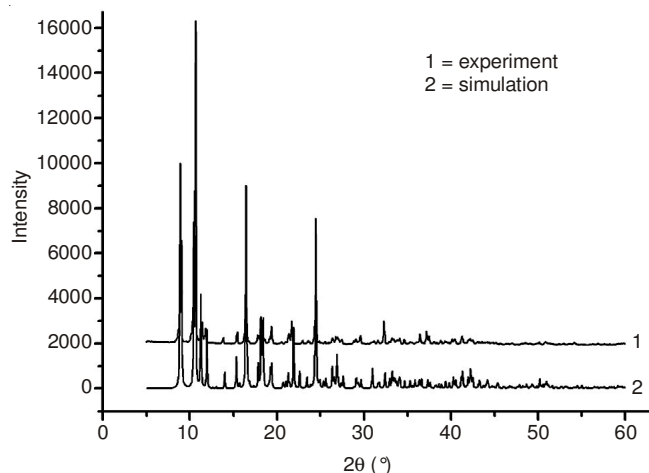


Fig. 4. Simulated and experimental X-ray powder diffraction pattern for **1**

structure of **1** should be the common (4, 4) net stacked by ABC mode along c axis, due to the influence of the ligand substitute group on the tacking mode, two apex of pyridine protrude into the adjacent layer approach to the methyl and quadrangle cavity accommodated two guest molecules from adjacent 2D net above and below, in order to fabricate the steady frameworks through  $\pi$ - $\pi$  reciprocity between pyridine and phenyl of another adjoining 2D network. In the previous reported structures, the similar framework synthesized by zinc and bdc in different solvent<sup>21</sup>, as a result, steady frameworks produced by the substitute group and axial ligands or guest molecules.

### Conclusion

In summary, we have successfully synthesized the coordination polymers  $[\text{Zn}(\text{dmbdc})(\text{py})]\cdot\text{NMP}]_{2n}$  (**1**) exhibit 2D (4,4) porous net with trinuclear zinc USBs and guest molecules NMP were accommodated in the quadrangular voids. The X-ray powder diffraction pattern and elemental analysis result show the pure phase was obtained by hot solution methods.

CCDC No. 970377 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* (please use the link below) by e-mailing data\_request@ccdc.cam.ac.uk, or by contacting: The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033. www.ccdc.cam.ac.uk/data\_request/cif

### ACKNOWLEDGEMENTS

The authors thank the NNSFC (Grant Nos. 20471050, 21071117 and 21277103) and College Outstanding Young Talent Fund of An-Hui Province (No: 2012SQRL198ZD).

### REFERENCES

1. W.Q. Kan, B. Liu, J. Yang, Y.Y. Liu and J.F. Ma, *Cryst. Growth Des.*, **12**, 2288 (2012).
2. A. Morozan and F. Jaouen, *Energy Environ. Sci.*, **5**, 9269 (2012).
3. X.X. Lv, S.F. Tang, L.J. Li, J.J. Cai, C. Wang, X.X. Xu and X.B. Zhao, *Eur. J. Inorg. Chem.*, **2013**, 5081 (2013).
4. J.W. Zhang, C.H. Gong, L.L. Hou, A.X. Tian and X.L. Wang, *J. Solid State Chem.*, **205**, 104 (2013).
5. R. Singh and P.K. Bharadwaj, *Cryst. Growth Des.*, **13**, 3722 (2013).
6. J. Zhao, D. Zhao, K. Peng, Y. Guo, S. Chen and J. Hu, *Transition Met. Chem.*, **38**, 771 (2013).
7. D.C. Zhong and T.B. Lu, *Sci. China Chem.*, **54**, 1395 (2011).
8. M.F. Wang, X.J. Hong, Q.G. Zhan, H.G. Jin, Y.T. Liu, Z.P. Zheng, S.H. Xu and Y.P. Cai, *Dalton Trans.*, **41**, 11898 (2012).
9. H.X. Sun, W.L. Xie, S.H. Lv, Y. Xu, Y. Wu, Y.M. Zhou, Z.M. Ma, M. Fang and H.K. Liu, *Dalton Trans.*, **41**, 7590 (2012).
10. L.N. Li, S.Y. Wang, T.L. Chen, Z.H. Sun, J.H. Luo and M.C. Hong, *Cryst. Growth Des.*, **12**, 4109 (2012).
11. P.O. Adelani and T.E. Albrecht-Schmitt, *Inorg. Chem.*, **50**, 12184 (2011).
12. H. Kwak, S.H. Lee, S.H. Kim, Y.M. Lee, B.K. Park, E.Y. Lee, Y.J. Lee, C. Kim, S.J. Kim and Y. Kim, *Polyhedron*, **27**, 3484 (2008).
13. G.X. Liu, Y.Q. Huang, Q. Chu, T. Okamura, W.Y. Sun, H. Liang and N. Ueyama, *Cryst. Growth Des.*, **8**, 3233 (2008).
14. C.J. Milios, T.C. Stamatatos and S.P. Perlepes, *Polyhedron*, **25**, 134 (2006).
15. F.K. Wang, S.Y. Yang, R.B. Huang and L.S. Zheng, *J. Chem. Crystallogr.*, **40**, 837 (2010).
16. G.M. Sheldrick, SADABS, version 2.05; University of Gottingen: Gottingen, Germany.
17. G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Determination, University of Gottingen, Germany (1997).