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Synthesis and Crystal Structure of a New Zn(II) Interpenetrating Complex Based on 1,4-bis(2-methylimidazol-1-yl)butane and 5-bromoisophthalic Acid

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### Synthesis and Crystal Structure of a New Zn(II) Interpenetrating Complex Based on 1,4-bis(2-methyl-imidazol-1-yl)butane and 5-bromoisophthalic Acid

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interpenetrating MOFs is to use long and low steric hindrance ligands.<sup>[14]</sup>

A new interpenetrating complex,  $[Zn(5-Br-ip)(bmib)]_n$  (5-Br-H<sub>2</sub>ip = 5-bromoisophthalic acid, bmib = 1,4-bis(2-methylimidazol-1-yl)butane), has been synthesised by hydrothermal reactions of  $Zn(NO_3)_2 \cdot 6H_2O$  and bmib in the presence of 5bromoisophthalic acid, and characterized by elemental analysis and single-crystal X-ray analysis. X-ray diffraction reveals that it belongs to the orthorhombic system, *P*nna space group, *a* = 8.7335(18) Å, *b* = 17.358(4) (10) Å, *c* = 14.769(3) Å,  $\alpha = \beta = \gamma =$ 90°, *F*(000) = 1064. R1 = 0.0389, *w*R2 = 0.0946. Complex 1 exhibits a fascinating 3-fold interpenetrating three-dimensional framework with the topological symbol of 6<sup>5</sup> \cdot 8.

Keywords 1, 4-bis(2-methyl-imidazol-1-yl)butane, crystal structure, hydrothermal synthesis, interpenetrating

### INTRODUCTION

As one of the major themes of supramolecular chemistry, entangled structures are common in nature, such as catenanes, rotaxanes, and molecular knots.<sup>[1,2]</sup> Owing to their numerous practical applications, physical and chemical properties, and aesthetic and usually complicated architectures and topologies, entangled metal-organic frameworks (MOFs) have received tremendous attention from chemists.<sup>[3-5]</sup> Among diverse entangled MOFs, interpenetration is the most familiar phenomenon. To date, considerable efforts have been invested in interpenetrating MOFs and a great many interpenetrating networks have been reported by many groups<sup>[6-9]</sup> and some comprehensive reviews have been made by Robson, Batten, and Ciani et al.<sup>[10-12]</sup> Summarizing from the large amount of reported works, we can draw a conclusion that long and low steric hindrance ligands will lead to larger voids that may result in high-fold interpenetrating structures.<sup>[13]</sup> Therefore, the effective strategy for constructing Inspired by the previous idea, we employed a long and flexible ligand 1,4-bis(2-methyl-imidazol-1-yl)butane (bmib) in the self-assembly with organic carboxylic acid 5-bromoisophthalic acid and Zn(II) ions to synthesize interpenetrating MOFs. Fortunately, a 3-fold interpenetrating three dimensional (3D) framework [Zn(5-Br-ip)(bmib)]<sub>n</sub> was obtained. The topological symbol is  $6^{5}$ ·8.

### **EXPERIMENTAL**

### **Materials and Physical Measurements**

All reagents used in the syntheses were of analytical grade. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Vario EL III (Germany, Elementar Analysensysteme GmbH) elemental analyzer. The infrared spectra (4,000–600 cm<sup>-1</sup>) were recorded by using KBr pellet on an Avatar 360 E. S. P. (Maryland, USA, Thermo-Nicolet) IR spectrometer. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer (Germany) equipped with graphite-monochromatized Mo*K* $\alpha$  radiation ( $\lambda$ = 0.71073 Å). Thermogravimetric analyses (TG) were carried out on a STA449C integration (Germany, NETZSCH) thermal analyzer. Fluorescent analyses were performed on a Hitachi F-4500 (Japan, Hitachi) analyzer.

### Syntheses of Complex 1

### $[Zn(5-Br-ip)(bmib)]_n$ (1)

This complex was prepared under hydrothermal conditions. A mixture of 5-Br-H<sub>2</sub>ip (24.3 mg, 0.1 mmol), bmib (21.8 mg, 0.1 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (29.7 mg, 0.1 mmol), KOH (5.6 mg, 0.2 mmol), and H<sub>2</sub>O (16 mL) was placed in a Teflon-lined stainless-steel vessel, heated to 160°C for 72 h, and then cooled to room temperature over 36 h. Yellow block crystals of **1** were collected by filtration, washed with water, and dried in air. Anal. Calcd. (%) for C<sub>20</sub>H<sub>21</sub>BrN<sub>4</sub>O<sub>4</sub>Zn: C, 45.61; H, 4.02; N, 10.64. Found (%): C, 45.85; H, 3.88; N, 10.75. IR (cm<sup>-1</sup>): 3125 (w), 2937 (w), 1624 (m), 1559 (w), 1423 (w), 1372 (w), 1335 (s),

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Empirical formula	$C_{20}H_{21}BrN_4O_4Zn$	
Formula weight	526.69	
Temperature (K)	296(2)	
Crystal system	Orthorhombic	
Space group	Pnna	
Unit cell dimensions	a = 8.7335(18)  Å	
	b = 17.358(4) Å	
	c = 14.769(3)  Å	
	$\alpha = \beta = \gamma = 90^{\circ}$	
V (Å <sup>3</sup> )	2238.9(8)	
Ζ	4	
$D_c (\text{Kg} \cdot \text{m}^{-3})$	1.563	
<i>F</i> (000)	1064	
GOF	1.017	
Crystal size (mm <sup>3</sup> )	$0.26 \times 0.09 \times 0.06$	
$\theta$ range for data collection ( <sup>0</sup> )	2.71-25.50	
Reflections collected	15560	
Independent reflections	$2094 (R_{\text{int}} = 0.0686)$	
Final <i>R</i> indices $(I > 2\sigma(I))$	$R = 0.0389, wR_2 = 0.0940$	
<i>R</i> indices (all data)	$R = 0.0667, wR_2 = 0.110$	
Largest diff. peak and hole (e $Å^{-3}$ )	0.661 and -0.435	

TABLE 1 Crystallographic data

$R_1 = [ F_0  -  F_c ]/ F_0 $ . $wR_2 =$	$  w( F_0^2   - $	$ F_{\rm c}^2 )^2$ / w	$V F_0^2 ^2]^{1/2}$
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1304 (w), 1280 (m), 1157 (w), 1123 (w), 1003 (w), 902 (w), 774 (w), 762 (m), 753 (m), 723 (s), 693(m).

## Crystallographic Data Collection and Structural Determination

Single-crystal X-ray diffraction analyses of the complex **1** were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) by using the  $\phi/\omega$  scan technique at room temperature. The structure were solved by direct methods with SHELXS-97.<sup>[15]</sup> Empirical absorption corrections were applied with SADABS program.<sup>[16]</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on  $F^2$  was carried out using SHELXL-97.<sup>[17]</sup>

NIB OZB OZB OIB Br

FIG. 1. Coordination environment of the Zn(II) ion in 1.

Table 1 shows crystallographic crystal data of **1**. Selected bond lengths and angles are listed in Table 2.

### **RESULTS AND DISCUSSION**

### **Crystal Structure Description**

 $[Zn(5-Br-ip)(bmib)]_n$  (1)

X-ray structural analysis shows that **1** crystallizes in the orthorhombic system, space group *P*nna, and features a 3-fold interpenetrating three-dimensional (3D) framework. Its asymmetric unit contains one Zn(II) ion, one bmib ligand, and one 5-Br-ip<sup>2–</sup> anion. The coordination environment around Zn(II) is shown in Figure 1. Each Zn(II) ion sits in a distorted tetrahedron geometry defined by two nitrogen atoms [Zn–N = 2.012 Å] of two bmib ligands and two oxygen atoms [Zn–O = 1.935 Å] from two separated 5-Br-ip<sup>2–</sup> anions. The Zn–O/N bond lengths are all consistent with corresponding bond lengths found in the literature.<sup>[3,18]</sup>

Each bmib ligand links two Zn(II) ions to form a 1D wavelike chain (Zn-bmib chain) with an adjacent Zn…Zn distance of 13.394 Å (Figure 2). The two carboxylic groups of 5-Brip<sup>2-</sup> take a uniform coordination mode, in a  $\mu_1$ - $\eta^1$ : $\eta^0$  fashion. Zn(II) ions are connected by 5-Br-ip<sup>2-</sup> anions to form a 1D chain (Zn-5-Br-ip<sup>2-</sup> chain) with a Zn…Zn distance of 10.587 Å (Figure 2). The combination of 1D chains of Zn-bmib and Zn-5-Br-ip<sup>2-</sup> leads to the formation of a 3D network (Figure 3).

Selected bold lengths (A) and bold angles (					
Zn(1)-O(1)#1	1.935(3)	O(1)#1-Zn(1)-N(1)	98.52(13)		
Zn(1)-O(1)	1.935(3)	O(1)-Zn(1)-N(1)	120.06(12)		
Zn(1)-N(1)	2.012(3)	O(1)#1-Zn(1)-N(1)#1	120.05(13)		
Zn(1)-N(1)	2.012(3)	O(1)-Zn(1)-N(1)#1	98.52(13)		
O(1)#1-Zn(1)-O(1)	116.97(19)	N(1)-Zn(1)-N(1)#1	103.3(2)		

 TABLE 2

 Selected bond lengths (Å) and bond angles (°)

Symmetry transformations used to generate equivalent atoms: #1 x, -y + 3/2, -z + 1/2; #2 - x - 1/2, -y + 1, z; #3 - x + 1, -y + 1, -z.



FIG. 2. (a) View of the 1D Zn–bmib wave-like chain. (b) View of the 1D Zn–5-Br-ip<sup>2–</sup> chain.

Owing to the long distance of Zn···Zn, there is a large unoccupied void space existing in the single 3D framework, which shows a possibility that 1 may display interpenetrating structural characteristics. As can be seen, the maximum dimensions (corresponding to the longest intracage Zn···Zn distances) are  $21.929 \times 18.171 \times 30.542$  Å. The potential voids are filled via mutual interpenetration of two other independent equivalent frameworks, generating a 3-fold interpenetrating 3D architecture (Figure 4). This feature can greatly enhance the stability of the whole structure.

To further demonstrate the overall 3D structure of **1**, we consider each Zn(II) ion as a four-connecting node, which is linked by two 5-Br-ip<sup>2–</sup> anions and two bmib ligands. Moreover, the bmib and 5-Br-ip<sup>2–</sup> anions are simplified as a linear linker. With further topological analysis by the OLEX program, the whole structure of **1** can be simplified to a 3-fold 3D framework with its topological notation of  $6^{5}$ .8.

### **Thermal Analysis**

To investigate the thermal stability of 1, their thermogravimetric analyses were examined in air atmosphere with the rate of  $10^{\circ}$ C min<sup>-1</sup> from room temperature to  $1000^{\circ}$ C. As shown



FIG. 3. Left: View of the 3D framework constructed by 1D Zn-bmib and Zn-5-Br-ip<sup>2-</sup> chains. Right: Schematic view showing the single 3D framework.



FIG. 4. Schematic view showing the 3-fold interpenetrated 3D topological network for **1**.

in Figure 5, complex 1 is stable up to about  $400^{\circ}$ C. Then the framework begins to disintegrate upon elevating the temperature.

### **Photoluminescence Properties**

The emission spectra of compound **1** have been investigated in the solid state at room temperature. The emission peaks of **1** are shown in Figure 6. Upon exciting at 333 nm, the maximum emission peaks at about 442 nm were observed for compounds **1**. Free 5-Br-H<sub>2</sub>ip and bmib ligands fluoresced in the solid state with their emission peaks at 500 nm<sup>[19]</sup> and 465 nm,<sup>[20]</sup> respectively. Compared to free ligands, complex **1** shows obvious blue



FIG. 5. TG curve of complex 1.



FIG. 6. Solid-state photoluminescent spectra of complex 1.

shifts. Because Zn(II) ions are fluorescent emissions that are tuned by the metal–ligand interactions and the deprotonated effect of the dicarboxylic ligands.<sup>[18,20]</sup>

### CONCLUSIONS

In summary, based on a long and flexible ligand 1,4-bis(2methyl-imidazol-1-yl)butane (bmib), a new interpenetrating complex [Zn(5-Br-ip)(bmib)]<sub>n</sub> has been successfully synthesised with Zn(II) salt in the presence of ancillary ligand 5bromoisophthalic acid. The complex manifests a 3D framework with large void space, which is penetrated by two other independent equivalent frameworks to give rise to 3-fold interpenetrating 3D architecture. Further systematic studies for the design and syntheses of interpenetrating polymers are underway in our laboratory.

### SUPPLEMENTAL MATERIAL

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 929613. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; E-mail: deposit@ ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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