

# Syntheses and Crystal Structures of Two New Complexes with 5-Bromoisophthalate and Bis(imidazole) Ligands

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Two new complexes, [Cu(5-Br-ip)(biim-5)]<sub>n</sub> (1) and [Ni(5-Br $ip_2(biim-4)]_n$  (2) [5-Br-H<sub>2</sub>ip = 5-bromoisophthalate; biim-4 = 1,4bis(imidazol)butane; biim-5 = 1,5-bis(imidazole)pentane], havebeen synthesized via hydrothermal reactions and characterized by elemental analysis and single-crystal x-ray analysis. Complex 1 belongs to the monoclinic system, P2(1)/c space group, a = 7.6055(19) $\dot{A}, b = 25.860(6) \dot{A}, c = 10.075(3) \dot{A}, \beta = 96.585(3)^{\circ}, F(000) = 1028,$  $R_1 = 0.0327$ ,  $wR_2 = 0.0820$ ; Complex 2 belongs to the triclinic system, *P-1* space group, a = 9.4766(12) Å, b = 11.5781(14) Å, c =14.1063(17) Å,  $\alpha = 73.5900(10)^\circ$ ,  $\beta = 71.8470(10)^\circ$ ,  $\gamma = 74.337(2)^\circ$ ,  $F(000) = 736, R_1 = 0.0662, wR_2 = 0.1626$ . In complex 1, the 5-Br-ip ligand takes the bidentate-bridging and bidentate-chelating modes to bridge the neighboring Cu(II) ions to yield a one-dimensional (1D) double chain with dinuclear Cu units. However, the 5-Br-ip ligand takes the bidentate-bridging modes to bridge the neighbouring Ni(II) ions to yield a 1D chain in complex 2. Both 1D chains in 1 and 2 are connected by biim-5 or biim-4 to form an infinite two-dimensional (2D) layer.

Keywords bis(imidazole), 5-bromoisophthalate, crystal structure, hydrothermal synthesis

# **INTRODUCTION**

The design and synthesis of metal-organic frameworks (MOFs) have attracted considerable attention because of their potential applications as function materials as well as their structural diversity and intriguing variety of topologies.<sup>[1-6]</sup> It is well known that carboxylate ligands play an important role in coordination chemistry, which may adopt diverse binding modes such as monodentate, chelating, and bridging in the *syn–syn, syn–anti*, and *anti–anti* configurations.<sup>[7–13]</sup> So far, a great many metal-carboxylate complexes, in the presence of rigid N-donor bridging ligands such as 4,4'-bipyridine and its derivatives have been designed and characterized widely. However, metal-carboxylate complexes containing flexible N-bridging ligands, especially bis(imidazole) ligands, have not

been well investigated. 1,4-Bis(imidazol)butane (biim-4) and 1,5-bis(imidazole)pentane (biim-5), bearing a longer methylene  $(-CH_2-)_4$  or  $(-CH_2-)_5$  skeleton, are good candidates for Ndonor linkers.<sup>[14–20]</sup> The flexible nature of the  $(-CH_2-)_4$  or  $(-CH_2-)_5$  spacer allows the molecules to bend and rotate freely when binding to metal centers so as to conform to the coordinative geometries of metal ions. In additon, 5-bromoisophthalate (5-Br-H<sub>2</sub>ip) may serve as a suitable building block to construct novel coordination polymers due to the existence of a noncoordinating electron-withdrawing Br group on the aromatic backbone, which will have a profound impact on the electron density of such a ligand and therefore different physical and chemical properties. In this contribution, 5-Br-H<sub>2</sub>ip, biim-4, and biim-5 are selected to react with Cu(II) and Ni(II) ions to obtain new MOFs. Herein, the syntheses and x-ray crystal structures of two coordination networks,  $[Cu(5-Br-ip)(biim-5)]_n$  (1) and  $[Ni(5-Br-ip)_2(biim-4)]_n$  (2), are reported.

### **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 elemental analyzer. The crystal determination was performed on a Bruker Smart Apex II CCD diffractometer equipped with graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å).

# **Syntheses of Complexes**

### $[Cu(5-Br-ip)(biim-5)]_n$ (1)

A mixture of 5-Br-H<sub>2</sub>ip (0.10 mmol, 24.5 mg), biim-5 (0.10 mmol, 20.4 mg), and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.10 mmol, 20 mg) in distilled water (15 mL) was placed in a Teflon-lined stainless-steel vessel, heated to 120°C for 3 days, and then cooled to room temperature over 24 h. Blue block crystals of **1** were obtained. Elem. anal. (%): calcd. for C<sub>19</sub>H<sub>19</sub>BrCuN<sub>4</sub>O<sub>4</sub> ( $M_r = 510.83$ ): C, 44.67; H, 3.75; N, 10.98; found: C, 44.58; H, 3.69; N, 10.90.

### $[Ni(5-Br-ip)_2(biim-4)]_n$ (2)

A mixture of 5-Br-H<sub>2</sub>ip (0.20 mmol, 49 mg), biim-4 (0.10 mmol, 19 mg), and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.10 mmol, 24.9 mg) in

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	Compound 1	Compound 2
Empirical formula	$C_{19}H_{19}BrCuN_4O_4$	C <sub>26</sub> H <sub>22</sub> Br <sub>2</sub> N <sub>4</sub> NiO <sub>8</sub>
Formula weight	510.83	737.01
Temperature (K)	296(2)	296(2)
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
	a = 7.6055(19)  Å	a = 9.4766(12)  Å
	b = 25.860(6)  Å	b = 11.5781(14)  Å
	c = 10.075(3) Å	c = 14.1063(17)  Å
Unit cell dimensions	$lpha=90~^\circ$	$\alpha = 73.5900(10)^{\circ}$
	$\beta = 96.585(3)^{\circ}$	$\beta = 71.8470(10)^{\circ}$
	$\gamma=90~^\circ$	$\gamma = 74.337(2)^{\circ}$
V (Å <sup>3</sup> )	1968.5(8)	1382.4(3)
Ζ	4	2
$D_c  ({\rm kg} {\rm m}^{-3})$	1.724	1.771
<i>F</i> (000)	1028	736
GOF	1.015	1.032
Crystal size (mm <sup>3</sup> )	$0.50 \times 0.22 \times 0.13$	$0.36 \times 0.24 \times 0.23$
$\theta$ range for data collection (°)	2.57~25.50	2.43~25.50
Reflections collected	14772	10587
Independent reflections	$3662(R_{\rm int} = 0.0335)$	$5109 (R_{\text{int}} = 0.0271)$
Final <i>R</i> indices $(I > 2\sigma(I))$	$R = 0.0327, wR_2 = 0.0820$	$R = 0.0662, wR_2 = 0.1626$
R indices (all data)	$R = 0.0452, wR_2 = 0.0899$	$R = 0.0879, wR_2 = 0.1773$
Largest diff. peak and hole (e $Å^{-3}$ )	1.160  and  -0.364	2.972 and -3.063

TABLE 1Crystallographic data for complexes 1 and 2

distilled water (15 mL) was placed in a Teflon-lined stainless steel vessel, heated to  $120^{\circ}$ C for 3 days, and then cooled to room temperature over 24 h. Green block crystals of **1** were obtained. Elem. anal. (%): calcd. for C<sub>26</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>4</sub>NiO<sub>8</sub> ( $M_r = 736.98$ ): C, 42.37; H, 3.01; N, 7.60; found: C, 42.28; H, 2.94; N, 7.52.

# Crystallographic Data Collection and Structures Determination

Single-crystal x-ray diffraction analyses of the two complexes 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 structures were solved by direct methods with SHELXS-97.<sup>[21]</sup> Empirical absorption corrections were applied with the SADABS program.<sup>[22]</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 leastsquares refinement on  $F^2$  was carried out using SHELXL-97.<sup>[23]</sup> The final R = 0.0327, wR = 0.0820 ( $w = 1/[\sigma^2(\text{F}_o^2) + (0.0355P)^2$ + 2.0850P], where  $P = (\text{F}_o^2 + 2\text{F}_c^2)/3$ ), S = 1.015, ( $\Delta \rho$ )<sub>max</sub> = 1.160, and ( $\Delta \rho$ )<sub>min</sub> = -0.364 e/Å^3 for **1**; and R = 0.0662, wR= 0.1626 ( $w = 1/[\sigma^2(\text{F}_o^2) + (0.0673P)^2 + 0.4338P$ ], where P $= (\text{F}_o^2 + 2c_c^2)/3$ ), S = 1.032, ( $\Delta \rho$ )<sub>max</sub> = 2.972, and ( $\Delta \rho$ )<sub>min</sub> =  $-3.063 \text{ e/Å}^3$  for **2**. Table 1 shows the crystallographic crystal data of **1** and **2**, and Table 2 shows their selected bond lengths and bond angles.



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

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 TABLE 2

 Selected bond lengths<sup>a</sup> (Å) and bond angles (°) for 1 and 2

Compound 1				
Bond	Distance	Bond	Distance	
Cu(1)-N(4)#1	1.981(3)	Cu(1)-O(1)	2.049(2)	
Cu(1)-N(1)	1.986(3)	Cu(1)-O(3)#3	2.280(2)	
Cu(1)-O(4)#2	1.998(2)	Cu(1)-O(2)	2.555(2)	
Angle	(°)	Angle	(°)	
N(4)#1-Cu(1)-N(1)	173.14(11)	O(4)#2-Cu(1)-O(1)	149.84(9)	
N(4)#1-Cu(1)-O(4)#2	96.83(11)	N(4)#1-Cu(1)-O(3)#3	87.65(10)	
N(1)-Cu(1)-O(4)#2	88.27(10)	N(1)-Cu(1)-O(3)#3	86.46(10)	
N(4)#1-Cu(1)-O(1)	88.53(10)	O(4)#2-Cu(1)-O(3)#3	107.17(9)	
N(1)-Cu(1)-O(1)	89.35(10)	O(1)-Cu(1)-O(3)#3	102.68(8)	
	Comp	ound 2		
Bond	Distance	Bond	Distance	
Ni(1)-O(2)	2.052(4)	Ni(1)-N(4)#2	2.069(5)	
Ni(1)-O(7)#1	2.054(4)	Ni(1)-O(4)#3	2.118(4)	
Ni(1)-N(1)	2.066(5)	Ni(1)-O(5)	2.117(4)	
Angle	(°)	Angle	(°)	
O(2)-Ni(1)-O(7)#1	93.09(16)	N(1)-Ni(1)-O(4)#3	86.60(19)	
O(2)-Ni(1)-N(1)	86.13(18)	N(4)#2-Ni(1)-O(4)#3	91.12(18)	
O(7)#1-Ni(1)-N(1)	176.90(19)	O(2)-Ni(1)-O(5)	96.40(17)	
O(2)-Ni(1)-N(4)#2	177.25(18)	O(7)#1-Ni(1)-O(5)	85.68(16)	
O(7)#1-Ni(1)-N(4)#2	87.27(18)	N(1)-Ni(1)-O(5)	91.42(18)	
N(1)-Ni(1)-N(4)#2	93.6(2)	N(4)#2-Ni(1)-O(5)	86.35(19)	
O(2)-Ni(1)-O(4)#3	86.13(16)	O(4)#3-Ni(1)-O(5)	176.68(17)	
O(7)#1-Ni(1)-O(4)#3	96.35(17)			

<sup>*a*</sup>Symmetry transformations used to generate the equivalent atoms: #1, -x + 2, y + 1/2, -z + 1/2; #2, x, y, z - 1; #3, -x + 2, -y + 2, -z + 1 for **1**; and #1, -x + 1, -y + 1, -z + 1; #2, x, y + 1, z; #3, -x, -y, -z + 1 for **2**.

# **RESULTS AND DISCUSSION**

# **Crystal Structure Description**

 $[Cu(5-Br-ip)(biim-5)]_n$ 

The x-ray structural analysis shows that 1 crystallizes in a monoclinic system, space group P2(1)/c and features a two-

dimensional (2D) network containing noncentrosymmetric dinuclea Cu units as nodes. As shown in Figure 1, the asymmetric unit of **1** consists of one Cu(II) ion, one 5-Br-ip ligand, and one biim-5 molecule. The geometry around the Cu(II) ion appears to be strong distorted octahedral, which is shown with the



FIG. 2. One-dimensional chain of 1 bridged by 5-Br-ip ligand.



FIG. 3. Two-dimensional layer of 1 connected by 5-Br-ip and biim-5 ligands.

angle O1–Cu1–O2 =  $56.430(74)^{\circ}$ . Four coordinated oxygen atoms from three 5-Br-ip ligands occupy the equatorial basal plane [Cu1-O1 = 2.049(2), Cu1-O2 = 2.555(2), Cu1-O3B =2.280(2), and Cu1–O4C = 1.998(2) Å], while two coordinated nitrogen atoms from two biim-5 molecules occupy the axial positions with an N1-Cu1-N4A angle of 173.14(11)°. The Cu-O and Cu-N bond lengths are in the range of 1.998(2)-2.555(2) and 1.9813(29)-1.9857(29) Å, respectively, which are in the normal range expected for such coordination bonds.<sup>[14,18]</sup> Two O atoms of each carboxylate group bridge two Cu(II) ions, and two such bridges form a eight-membered noncentrosymmetric dinuclear ring with a Cu...Cu nonbonding distance of 4.6552(11) Å. Further, such ring units are bridged by the 5-Br-ip ligands to yield a one-dimensional (1D) double chain (Figure 2). Then the neighboring 1D chains are linked by biim-5 molecules to form an infinite 2D sheet (Figure 3). The biim-5 molecule adopts a bidentate-bridging conformation mode with the dihedral angle between the two imidazole rings of 86.06°, suggesting that these imidazole rings of each flexible ligand are almost perpendicular to each other. The Cu-Cu separation across the biim-5 molecule is 13.0 Å.

### $[Ni(5-Br-ip)_2(biim-4)]_n$

X-ray analysis reveals that the asymmetric unit of 2 consists of one central Ni(II) ion, two 5-Br-ip ligands, and one biim-4 molecule. The coordination environment around the Ni(II) ion can be described as a distorted octahedral [NiO<sub>4</sub>N<sub>2</sub>] coordination geometry (as shown in Figure 4). Each Ni(II) ion is sixcoordinated with two nitrogen atoms from two biim-4 molecules and four oxygen atoms from four 5-Br-ip ligands. The Ni–O and Ni–N bond lengths are in the range of 2.052(4)–2.118(4) and 2.066(5)–2.069(5) Å, respectively, which are all within the normal range generally found in the literature.<sup>[16]</sup> In **2**, the 5-Br-ip ligand takes the bidentate-bridging modes to bridge the neighboring Ni(II) ions to yield a 1D chain (Figure 5). Furthermore, these 1D chains are linked by biim-4 molecules to form an infinite 2D sheet (Figure 6). The biim-4 molecule adopts a bidentate-bridging conformation mode with the dihedral angle



FIG. 4. Coordination environment of the Ni(II) ion in 2.



FIG. 5. One-dimensional chain of 2 bridged by 5-Br-ip ligand.



FIG. 6. Two-dimensional layer of 2 connected by 5-Br-ip and biim-4 ligands.

between the two imidazole rings of  $21.00^{\circ}$ . The Ni…Ni separation across the biim-4 molecule is 11.6 Å.

# **CONCLUSIONS**

In summary, we have successfully prepared two new 5-Br-ip coordination polymers with Cu(II) and Ni(II) salts in the presence of flexible bis(imidazole) ligands. The two complexes both exhibit 2D networks constructed from 5-Br-ip and bis(imidazole) ligands. However, the two 1D chains are different. This may be ascribed to the effect of metal ions and the different flexibility of the two bis(imidazole) ligands, which results in the different coordination modes of the 5-Br-ip ligands. Further systematic studies for the design and syntheses of such polymers with polycarboxylate and bis(imidazole) ligands are underway in our laboratory.

### SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 780633 and 815227. 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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