TWO NEW 1D COORDINATION POLYMERS: SYNTHESES, STRUCTURES AND PROPERTIES

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ABSTRACT. Two new coordination polymers, namely, $[Zn(bi)(Cl)_2]_n$ (**1**) and $[Cu(L)_2(bib)(H_2O)_2]_n$ (**2**) (bi = 4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl; L = 4-(2-(4-(methoxycarbonyl)phenoxy)ethoxy)benzoic acid and bib = 2,3-bis(4-pyridyl)butane), are synthesized and characterized. Both of **1** and **2** have 1D covalent chains, which show different conformally chain feature. 2D supremolecular rhombic and rectangle motifs are observed in **1** and **2**, respectively. The O–H⋯O and C–H⋯Cl hydrogen-bonding interactions play a significant role in promoting the diversity of structural patterns.

**KEY WORDS**: Structure, Supramolecular interaction, Luminescence

INTRODUCTION

During the last decade, the number of studies related to the synthesis of crystalline porous organic–inorganic hybrid materials has grown rapidly [1-3]. The structural diversity and property employments of carboxylate polymers have been expanded by the incorporation of neutral organodiimines such as 4,4'-bipyridine [4]. The structural rigidity of benzene dicarboxyalte/N-conatining subunits can be useful to construct of porous materials, flexible subunits can form different motifs due to their ability to access numerous energetically conformations. However, flexible carboxylate and N-donor scaf-folded coordination polymers have received less attention. Even so, the prediction and synthesis of the solid-state architectures still remain a long-term challenge for the chemists [5-10].

On the other hand, the development of supramolecular assembled chemistry has allowed the possibility to rationally design and prepare supramolecular networks. Meanwhile, many investigations indicate that the weak interaction is a powerful force for supramolecular structural assembly in crystal engineering [11-14]. Based on above consideration, we report here the syntheses, structural characterization, and spectral analyses of two new coordination polymers based on three types of organic ligands (Scheme 1), namely, $[Zn(bi)(Cl)_2]_n$ (**1**) and $[Cu(L)_2(bib)(H_2O)_2]_n$ (**2**). The L was generated from 1,3-bis(4-carboxy-phenoxy)propane under hydrothermal condition in presence of copper salt.
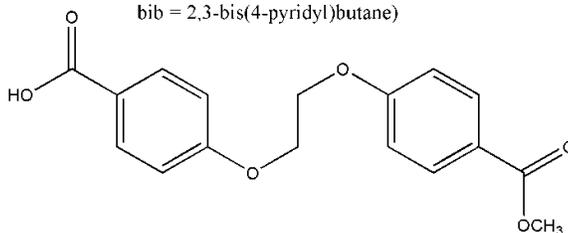
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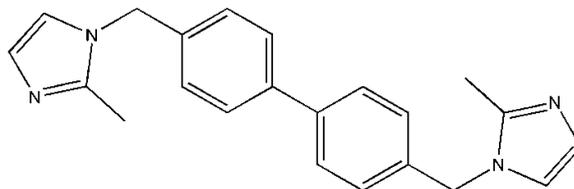
bi = 4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl
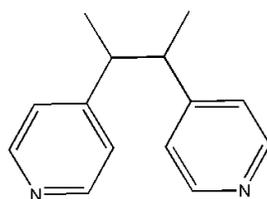
bib = 2,3-bis(4-pyridyl)butane)

L = 4-(2-(4-(methoxycarbonyl)phenoxy)ethoxy)benzoic acid

Scheme 1. The three types of organic ligands in this work.

EXPERIMENTAL

Materials and method

All reagents were purchased from commercial sources and used as received. IR spectra were recorded with a Perkin–Elmer Spectrum One spectrometer in the region 4000–400 cm^{-1} using KBr pellets. TGA were carried out with a Metter–Toledo TA 50 in dry dinitrogen (60 mL.min^{-1}) at a heating rate of 5 ^{o}C min^{-1}. X-ray powder diffraction (XRPD) data were recorded on a Rigaku RU200 diffractometer. Luminescence spectra data were recorded at an Edinburgh FLS920 phosphorimeter.

X-Ray crystallography

Single crystal X-ray diffraction analyses of the three compounds were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å) by using ϕ/ω scan technique at room temperature. The intensities were

corrected for Lorentz and polarization effects as well as for empirical absorption based on multi-scan techniques; all structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [15]. Absorption corrections were applied by using multi-scan program SADABS [16]. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The water hydrogen atoms were located from difference maps and refined with isotropic thermal parameters 1.5 times those of their carrier atoms. The compound **2** was weakly diffractors giving poor data and that we were unable to obtain better crystals despite attempt to do so, assuming that was the case. Table 1 shows crystallographic data of **1–2**. Selected bond distances and bond angles are listed in Table 2. CCDC: 971716-971717. These data can be obtained free of charge via www.ccdc. cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223–336–033; or deposit@ccdc.cam.ac.uk).

Table 1. The crystallographic data of **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{22}H_{22}Cl_2N_4Zn$	$C_{48}H_{50}CuN_2O_{14}$
Formula mass	478.71	942.44
Crystal system	Orthorhombic	Triclinic
Space group	*P b c n*	*P-1*
a [Å]	8.899(4)	7.3012(5)
b [Å]	14.460(7)	11.7373(7)
c [Å]	16.930(8)	13.9407(9)
α [°]	90	74.686(5)
β [°]	90	77.195(5)
γ [°]	90	84.677(5)
V [Å³]	2178.5(18)	1122.85(13)
Z	2	1
d_{calcd} [g·cm⁻³]	1.460	1.394
μ [mm⁻¹]	1.388	0.557
$F(000)$	984	493
Reflections collected	10426	14498
$R_{(int)}$	0.0356	0.0788
R_1, wR_2 [$I>2\sigma(I)$]	0.0370, 0.1199	0.0619, 0.1417
R_1, wR_2 (all data)	0.0527, 0.1369	0.1419, 0.1784

Synthesis of the complexes

$[Zn(bi)(Cl)_2]_n$ **(1)**. A mixture of $ZnCl_2 \cdot 5H_2O$ (0.0512 g), H_2bce (0.0285 g), bi (0.0204 g), deionised water (10 mL) and CH_3OH (5 mL) was stirred in air. The pH of the resulting solution was adjusted to 7 using dilute NaOH (1 M) and kept at 160 °C for 72 h at oven, and then cooled down to 25 °C. The resulting crystals formed were filtered off, washed with water and dried in air. $C_{22}H_{22}Cl_2N_4Zn$. Calcd: C, 55.19; N, 11.70; H, 4.63. Found C, 55.38; N, 11.49; H, 4.56. IR (KBr, cm⁻¹): 3019(m); 1595(m); 1434(s); 1284 (m); 1105(m); 843(s); 756(s).

$[Cu(L)_2(bib)(H_2O)_2]_n$ **(2)**. A mixture of $Cu(NO_3)_2 \cdot 6H_2O$ (0.0411 g), H_2L (0.0291 g), bib (0.0254 g), deionised water (10 mL) and CH_3OH (5 mL) was stirred in air. The pH of the resulting solution was adjusted to 7 using dilute NaOH (1 M) and kept at 160 °C for 72 h at oven, and then cooled down to 25 °C. The resulting crystals formed were filtered off, washed with water and dried in air. $C_{48}H_{50}CuN_2O_{14}$(942.44) Calcd: C, 61.17; N, 2.97; H, 5.35. Found: C, 60.88; N,

2.71; H, 5.20. IR (KBr, cm^{-1}): 3428(vs), 3085(m); 1659(m); 14211(s), 1120(m), 1011(m), 859(m), 711(m).

RESULTS AND DISCUSSION

*[Zn(bi)(Cl)$_2$]$_n$ (**1**)*

As shown in Figure 1a, each ligand coordinates to two Zn(II) ions and each Zn(II) ion is coordinated by two bi to generate a 1D zigzag chain. The Zn(II) is in a distorted tetrahedral geometry with its coordination sphere completed by two Cl anions. The two Zn(II)-Cl distances are longer than that of Zn-N bond distances (Table 2). Each bi ligand possesses a crystallography inversion center that is situated in the middle of the central benzene ring. As a result, each adopts an *anti-syn* conformation. The imidazole rings are almost perpendicular to the benzene ring, with a dihedral angle of 83.55º. The adjacent Zn(II) are connected by bi into a 1D helical chain, as shown in Figure 1b-1d.

Table 2. Selected bond distances (Å) and angles (°).

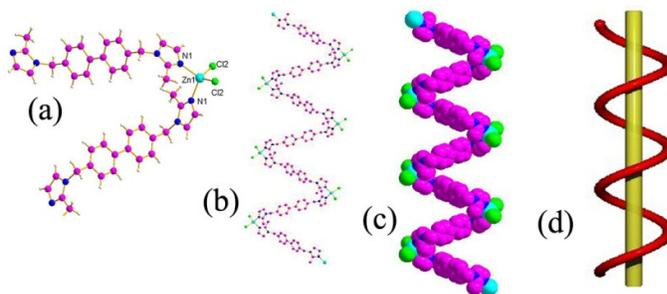| **1**			
Zn1-N1#1	2.011(3)	Zn1-Cl1#1	2.2310(10)
N1-Zn1-N1	105.11(15)	N1-Zn1-Cl1	103.92(8)
Cl1-Zn1-Cl1	114.24(6)		
#1: -x, y, -z+1/2.			
2			
Cu1-O1#1	1.952(3)	Cu1-N1#1	1.994(3)
Cu1-O1W#1	2.621(5)	O1-Cu1-O1	180
O1W-Cu1-O1W	180	N1-Cu1-O1	91.26(13)
N1-Cu1-N1	180		
#1: -x, 1-y, 1-z.			

Figure 1. (a) View of the coordination geometry for Zn(II) ion; (b) the 1D helical chain; (c) the filling result for 1D chain; and (d) the schematic picture for 1D helical chain.

The hydrogen contacts mainly determine the crystal packing shown in Figure 2a. These parallel polymeric chains are connected through extensive hydrogen bonds C–H···Cl to form a 2D supramolecular net (Figure 2b).
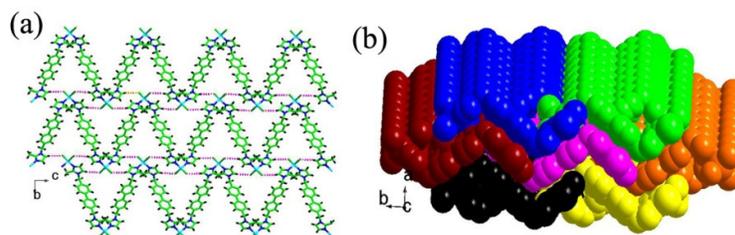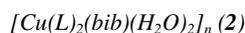
Figure 2. (a) View the 2D grid sheet constructed by supramolecular interactions; (b) view of the packing interaction among adjacent sheets.

[Cu(L)$_2$(bib)(H$_2$O)$_2$]$_n$ (2)

X-ray crystallographic data reveal that complex **2** is made up of a one-dimensional square-wave-like chain. Here each Cu(II) atom is coordinated by two oxygen atoms from two synmmetric water molecules, two carboxyl oxygen atoms (O1, O1A) and two nitrogen atom from bib ligands, forming a octahedral coordination geometry (Figure 3). The Cu–O bond lengths range from 1.952(3) to 2.620(8) Å, and the Cu–N distance is 1.994(3) Å, comparable to those in the six coordinated Cu(II) complexes. The L was in situ generated from 1,3-bis(4-carboxy-phenoxy)propane. One carboxyl group in 1,3-bis(4-carboxy-phenoxy)propane has joined a methylation process in the presence of copper resource, in which has been observed in reported complexes.
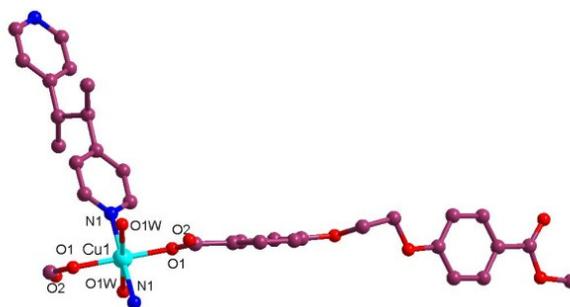

Figure 3. View of the coordination mode for Cu(II) atom in **2**.

The bib taking as monodentate mode binds to Cu(II) ions into a 1D chain. These kernels chains are oriented parallel to the *b* crystal axis. More interestingly, a 2D supramolecular motif could be formed by the extensive hydrogen bonds O–H···O between coordinated water molecule and methoxy group as shown in Figure 4.
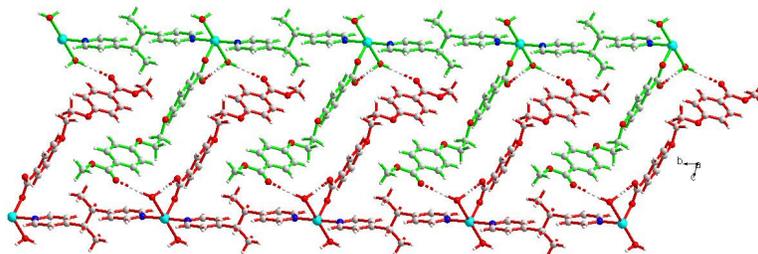
Figure 4. View of the 2-D grid network directed by O-H···O hydrogen bonding interactions.

Barbour and his co-workers reported a series of $[M_2Cl_4bi_2]\cdot 2CH_3OH$ (M = Cd, Zn and Co), which each complex the two metal ions are tetrahedrally coordinated to two chloride anions and two C-shaped bridging ligands. Metallocycles stack to form columns, and that this packing mode creates solvent-filled pockets between adjacent metallocycles [17-18]. Each metallocycle shares cavities with both of its neighbors. The difference between the **1** and $[M_2Cl_4bi_2]\cdot 2CH_3OH$ may be induced by the template effect. Although the 1,2-bis(4-carboxy-phenoxy)ethane (bce) ligand does not crystallize and coordinates to metal ions from the compound. But if the bce does not use as starting material, the crystal samples could not be obtained. Thus, the bce molecule may take as template agent in self-assembly of the title compound **1**.

*TGA and XPRD analysis of complexes **1** and **2***

To study the stability of the polymer, thermogravimetric analyses (TGA) of complexes **1-2** were performed (Figure S1). The TGA result of **1** shows only one weight loss step. The weight loss began at 110 °C and completed at 755 °C. The observed weight loss of 72.4 % is corresponding to the loss of the bi (calcd 71.6%). The final mass remnant of 22.8% may be consistent with ZnO (17.2% predicted). The TGA result of **2** shows two weight loss steps. The first weight loss began at 65 °C and completed at 175 °C, corresponding to the loss of coordinated water molecules (calcd 3.8 %). Soon after, the elimination of L and bib ligands was observed. The remnant at 780 °C (26.2%) is indicative of a mixture of $CuCO_3$ and CuO.
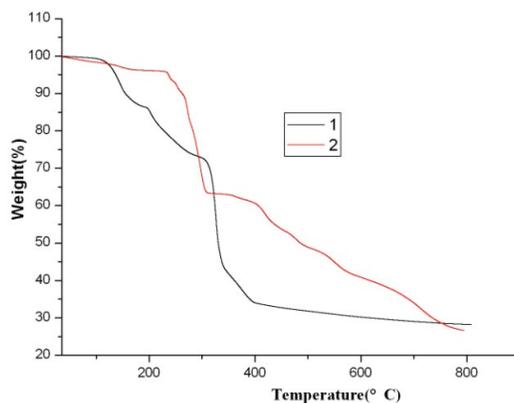

Figure S1. The diagram of TGA for compounds **1** and **2**.

Additionally, to confirm the phase purity and stability of compound **1**, the original samples were both characterized by X-ray powder diffraction (XRPD). The XRPD experimental and computer-simulated patterns of **1-2** are shown in Figure S2. Although the experimental patterns have a few unindexed diffractions lines and some are slightly broadened in comparison to those simulated from single-crystal models, it can still to be considered that the bulk synthesized materials and as-grown crystal are homogeneous for compounds **1-2**.
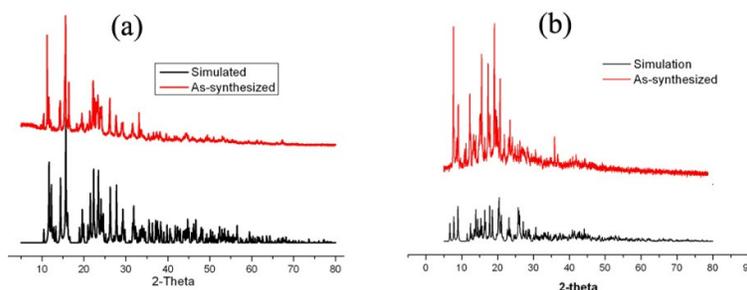

Figure S2. Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized product in compounds **1** and **2**.

Coordination polymers with d^{10} metal centers have been investigated for their fluorescent properties and potential applications as fluorescent-emitting materials, such as light-emitting diodes (LEDs) [19]. Therefore, the complex **1** were studied in the solid-state at room temperature. Excitation of the microcrystalline sample at 312 nm leads to the generation of fluorescent emission, with the peak maxima occurring at 371 nm for **1**, as shown in Figure 5. To further understand the origin of these emission bands, the ligand bi displays photoluminescence with emission maximum at 323 nm (λ_{ex} = 300 nm) [20]. Due to its d^{10} electronic configuration, Zn(II) is difficult to oxidize or reduce, so the emission here is neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer. The profile and position of the emission band of **1** is similar to those observed in the free bi ligand, they may be assigned mainly to the intraligand transition of bi which is modified by metal coordination. The emission in the blue region suggests that **1** could be taken as potential blue-light-emitting materials [21].
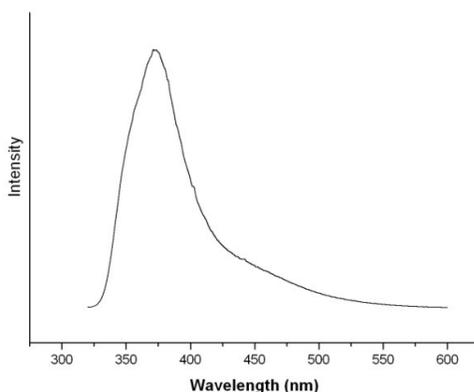

Figure 5. View of the fluorescence spectrum of **1** at room temperature.

CONCLUSION

In summary, two new 1D polymers were constructed by organic linkers. The difference in the structures reveals that the auxiliary ligand may play a role in modulating the resulting motifs. Further systematic work towards fabricating more polymers with interesting structures and functionalities using flexible ligands is in progress.

ACKNOWLEDGMENTS

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