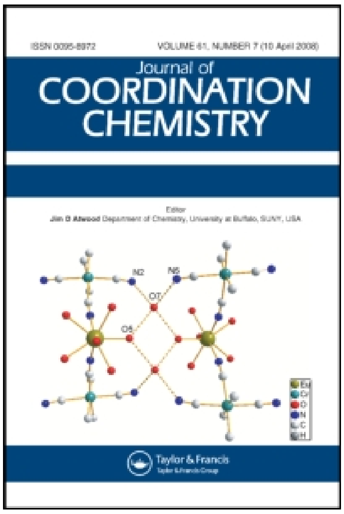

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Synthesis, crystal structure, and fluorescence of a 2-D coordination polymer

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Synthesis, crystal structure, and fluorescence of a 2-D coordination polymer

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A 2-D coordination polymer with mixed ligands, $[Zn_2(BDC)(4,4'\text{-bipy})(HCOO)_2]$ (**1**) (BDC, 1,4-benzenedicarboxylate; 4,4′-bipy, 4,4′-bipyridine), has been synthesized by solvothermal reaction. Compound **1** provides the first coordination polymer structure constructed by bridging BDC, 4,4′-bipy, and formate. Both BDC and 4,4′-bipy link zincs alternatively, resulting in a zigzag coordination chain; adjacent chains are further linked by formates to form an infinite extended 2-D folding screen layer. The synthesis mechanism and fluorescence property are discussed.

Keywords: Coordination polymer; Solvothermal condition; Mixed-ligand; Photoluminescent property

1. Introduction

There is an upsurge of interest in the synthesis of metal-organic coordination polymers due to their various structures and potential applications in catalysis, gas absorption, nonlinear optics, luminescence etc. [1–4]. Versatile synthetic approaches for the assembly of target structures from metal ions as connectors and organic ligands as linkers have been developed. Solvothermal technique has been found to be an effective route to obtain various metal-organic coordination polymers [5, 6]. Solvothermal reactions provide a closed system and higher pressure that may be useful for crystallization. Although a number of coordination polymers with intriguing architectures and interesting properties have been reported, a rational strategy to synthesize desired solid-state materials is still a great challenge [7, 8]. In addition, coordination polymers with mixed ligands might display useful guest-transport, fluorescence, and other properties [9–11]. Compounds with two ligands have been reported; however, structures with three or more ligands have rarely been observed.

In this article, we synthesize a zinc coordination polymer with solvothermal reaction. 1,4-benzenedicarboxylate (BDC) and 4,4′-bipyridine (4,4′-bipy) are bridging ligands that can stabilize structures. *N*, *N*-dimethylformamide (DMF) and nitrate are employed

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as solvent and the source of metal ion, respectively. We isolate a 2-D coordination polymer with three ligands [$Zn_2(BDC)(4,4'\text{-bipy})(HCOO)_2$] (**1**). To our knowledge, **1** represents the first metal-organic coordination polymer structure in which three ligands (BDC^{2-}, 4,4′-bipy, and $HCOO^-$) adopt bridging modes connecting metal centers. The formate that comes from DMF hydrolization coordinates to zinc making the whole structure stable [12]. In addition, **1** exhibits blue photoluminescence in the solid state at room temperature.

2. Experimental

2.1. *Materials and methods*

All reagents and solvent were purchased from commercial sources and used as received. Elemental analyses (C, H, and N) were performed on a Perkin Elmer 2400 CHN elemental analyzer. IR spectra were recorded in the range of 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Powder X-ray diffraction measurements were performed on a Rigaku D/MAX-3 instrument with Cu-Kα radiation in the angular range $2\theta = 3$–60° at 293 K. Thermalgravimetric analysis (TGA) was performed on a Perkin Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ C\,min^{-1}$. Excitation and emission spectra of **1** were obtained on a SPEX FL-2T2 spectrofluorometer equipped with a 450-W xenon lamp as the excitation source.

2.2. *Preparation of [$Zn_2(BDC)(4,4'\text{-bipy})(HCOO)_2$]*

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.150 g, 0.5×10^{-3} mol), H_2BDC (0.030 g, 0.2×10^{-3} mol), 4,4′-bipy (0.031 g, 0.2×10^{-3} mol) in DMF (8 mL) was sealed in a 23 mL Teflon-lined autoclave and heated at 85°C for 5 days. Then, it was cooled to room temperature at a rate of $1.5^\circ C\,h^{-1}$. After being washed with DMF several times, **1** was collected as colorless leaf-shaped crystals with a yield of about 48% (based on Zn). Formula $Zn_2C_{20}H_{14}N_2O_8$, Elemental analysis (%): C, 46.55 (Calcd 46.48); H, 5.74(5.91); N, 11.39(11.12). FT-IR (KBr pellets) 1611(vs), 1565(vs), 1431(s), 1356(m), 810(m), 741(w), 642(w).

2.3. *X-ray crystallography*

Diffraction intensities for **1** were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo-Kα monochromatic radiation ($\lambda = 0.71073$ Å) at 283 K. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography. Empirical absorption corrections were applied. The structures were solved by direct method and refined by full-matrix least-squares on F^2 using the SHELXTL-97 crystallographic software package [13, 14]. All non-hydrogen atoms were refined anisotropically. The crystal data and structure refinement results are summarized in table 1. The experimental and simulated X-ray powder diffraction patterns

Table 1. Crystal data structure refinement parameters for **1**.

Empirical formula	$Zn_2C_{20}H_{14}N_2O_8$
Formula weight	541.12
Crystal system	Orthorhombic
Space group	*pbcn*
θ range for data collection (°)	3.02–27.47
Unit cell dimensions (Å, °)	
a	18.543(4)
b	9.3920(1)
c	11.399(2)
α	90.00(0)
β	90.00(0)
γ	90.00(0)
Volume (Å^3), Z	1985.2(7), 8
F(000)	1082.74
Calculated density (g cm^{-3})	1.804
Absorption coefficient (mm^{-1})	2.470
Reflections collected	17,548
Independent reflection	2253[R(int) = 0.0616]
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1{}^{a} = 0.0382$, $wR_2{}^{b} = 0.0844$

$^{a}R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.
$^{b}wR_2[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

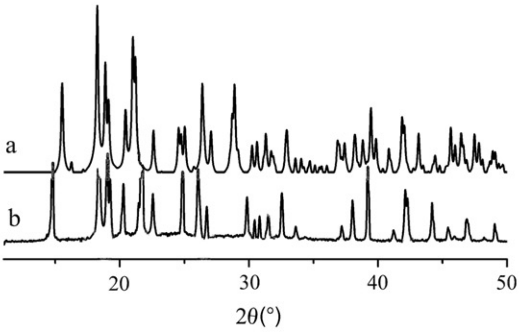

Figure 1. The XRPD patterns of **1**: simulated (a) and experimental (b).

(XRPD) are shown in figure 1. The main diffraction peaks on experimental and simulated patterns match well in position, indicating its phase purity.

3. Results and discussion

3.1. *Synthesis and structure*

Compound **1** has been synthesized with zinc nitrate, BDC, 4,4′-bipy, and DMF as solvent, heating at 85°C. Although many zinc coordination compounds have been published [11, 15–17], synthesis of **1** is more attractive. DMF plays an important role in the formation of formate, not only serving as the solvent for crystallization. We presume that the hydrolization of DMF could attribute to two points, in our experiment condition. First, although the reaction temperature is mild, the hydrolization of zinc ions gives the character of weak base. The rate of hydrolysis increases at basic condition. Second, formate coordinates to zinc, shifting the hydrolysis balance. Therefore, both the formate and zinc ions are catalysts for the hydrolization of DMF. The equation of the hydrolysis mechanism is shown below:

$$(CH_3)_2NCOH + H_2O \longrightarrow (CH_3)_2NH + HCOOH$$

$$2Zn^{2+} + 2HCOO^- + BDC^{2-} + 4{,}4'\text{-bipy} \xrightarrow[85^\circ C,\,5\text{ days}]{DMF} Zn_2(BDC)(4{,}4'\text{-bipy})(HCOO)_2$$

Parallel experiments have been performed in order to find optimum synthesis conditions. We vary the reaction time from 1 to 5 days; when the reaction time is 2 days, we obtain colorless block-shaped crystals which have been reported in [18]. Formate does not coordinate to zinc in this structure. The long reaction time is beneficial for the formation of **1**.

The structure of **1** is a 2-D polymer with three kinds of ligands bridging between the zinc ions. The coordination environment of the metal center for **1** is presented in figure 2. Each zinc is bonded to three oxygens from one BDC, two different formates and one nitrogen from one 4,4′-bipy to complete a distorted tetrahedral geometry. The Zn–O bond distances range from 1.939(2) to 1.995(2) Å and the N–O bond distance is 2.057(3) Å. Both BDC and 4,4′-bipy link zinc alternatively into a zigzag coordination chain running along the *b*-axis (figure 3a), and adjacent chains are further linked by formate to form a 2-D folding screen layer extending throughout the *ac*-plane (figure 3b). The closest Zn···Zn distance between adjacent chains is 4.699(1) Å, indicating the lack of any direct metal–metal interaction.

3.2. *IR spectroscopy*

The infrared spectrum (Supplementary material) shows characteristic bands of the ligands, fully supporting the organic components. The absorptions for the

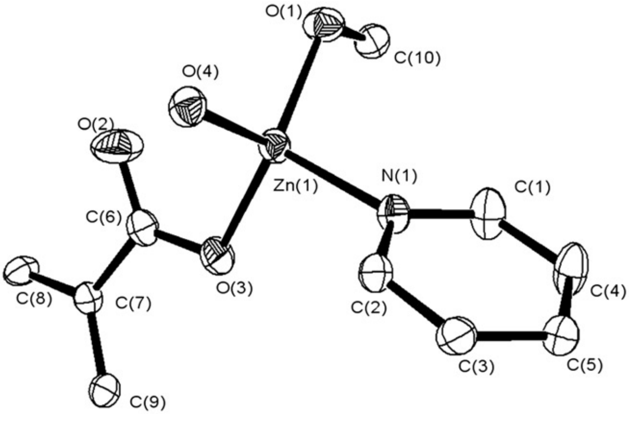

Figure 2. The coordination environment of zinc in **1**.

antisymmetric stretching vibrations $\nu_{as}(CO_2^-)$ of the carboxyl appear at $1565\,cm^{-1}$, and symmetric stretching vibrations $\nu_{as}(CO_2^-)$ are observed at $1356\,cm^{-1}$. The carboxyl frequencies shifted to lower values compared with those of free aromatic acid indicate changes upon coordination to the metal ion [19, 20]. Bands located around 1611 and $1431\,cm^{-1}$ strongly support the existence of the coordinated N-donor ligands arising from $\nu_{C=N}$ [21].

3.3. *Thermogravimetric analysis*

The thermal stability (under continuous N_2 flow) was investigated between ambient temperature and 600°C (Supplementary material). The TGA curve of **1** exhibits two discontinuous weight loss stages below 475°C, the first from ambient temperature to 193°C, of 36.03% (Calcd 37.15%), which corresponds to the release of a 4,4′-bipy and a formate. The second weight loss is 30.22% (Calcd 30.31%) in the temperature range of 193–475°C, corresponding to the release of BDC. The sample decomposes to zinc oxide at higher temperature.

3.4. *Photoluminescence*

Previous studies have shown that coordination polymers containing zinc exhibit photoluminescent properties [22–24]. Thus, the fluorescence of **1** has been investigated in the solid state at room temperature. As shown in figure 4, **1** exhibits blue photoluminescence with an emission maximum at *ca* 406 upon excitation at 350 nm. According to the reported literature, free H_2BDC exhibits fluorescent emission at 393 nm ($\lambda = 347$ nm) [25]. For **1**, the main peak of emission is red-shifted compared with free H_2BDC. The emission may be assigned as ligand-to-metal charge transition (LMCT). Blue photoluminescence from colorless crystals under ultraviolet (UV)

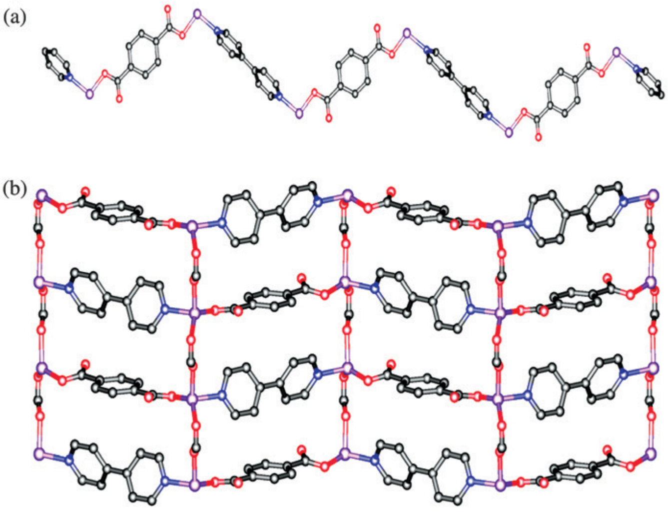

Figure 3. (a) The 1-D zigzag coordination chain of **1** and (b) 2-D folding screen layer of **1**.

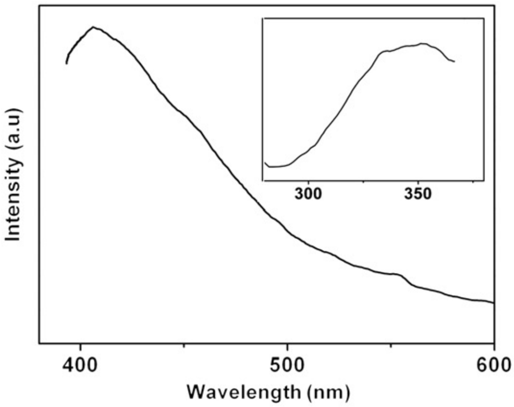

Figure 4. Fluorescence spectrum for **1** in the solid state at room temperature (inset: excitation spectrum of **1** in the solid state).

irradiation (365 nm) is so intensive that can be observed macroscopically (Supplementary material).

4. Conclusion

We successfully obtained a 2-D folding screen layer coordination polymer under solvothermal conditions. Compound **1** exhibits blue fluorescent emission that may be a candidate for photoactive material. In addition, DMF slowly hydrolyzes to formate; by controlling the reaction temperature and time, compound **1** can be obtained. Formate coordinating to zinc leads to complete hydrolysis of DMF. This strategy will be employed to synthesize more novel structures.

Supplementary material

CCDC-723836 for **1** contains supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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