



Room temperature syntheses, crystal structures and properties of two new heterometallic polymers based on 3-ethoxy-2-hydroxybenzaldehyde ligand



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ABSTRACT

Two new heterometallic coordination polymers $[\text{ZnNa}(\text{ehbd})_2(\text{N}_3)_n]_n$ (**1**) and $[\text{Cu}_3\text{Na}_2(\text{ehbd})_2(\text{N}_3)_6]_n$ (**2**) (*Hehbd* is 3-ethoxy-2-hydroxybenzaldehyde) have been synthesized under room temperature and structurally characterized by elemental analysis, IR, UV, TG and single crystal X-ray diffraction. Complex **1** crystallizes in the orthorhombic space group *Pbca*, showing a one-dimensional (1-D) chain. Complex **2** crystallizes in the triclinic space group *Pt*, constructing a heterometallic 2D layer structure. Luminescent properties and magnetic properties have been studied for **1** and **2**, respectively and the fluorescence quantum yield of **1** is 0.077.

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1. Introduction

The research on coordination polymers (CPs) or metal–organic framework has recently attracted a great deal of attention within the fields of crystal engineering and inorganic, coordination, and material chemistry, particularly in view of the structural diversity and promising applications of compounds such as multifunctional materials. [1–10]. In contrast to the very broad use of rare earth or transition metals as nodes in the construction of coordination polymers [11,12], through *s*-block metal centers that have versatile coordination and supramolecular behaviors, nontoxic nature, and widespread presence in diverse natural environments and living systems, the application of the common *s*-block metal centers (i.e. Li, Na, K, Mg, Ca) for such a purpose has been explored to a lesser extent [13–20]. Moreover, heterometallic coordination polymers incorporating both transition and alkaline or alkaline earth metals are even less common [13–22], although the introduction of two different metal centers can alter the structural, topological, and physicochemical properties of the resulting network materials.

An effective and facile approach for the synthesis of such complexes is still the appropriate choice of well-designed organic ligands as bridges or terminal groups with transition metal ions and

alkali metal ions as nodes. As well known, 2-hydroxy-3-methoxybenzaldehyde has been reported of four coordination modes which are $\mu_3:\eta^2:\eta^2:\eta^1$ (Scheme S1a) [23], $\mu_1:\eta^1:\eta^1$ (Scheme S1b) [24,25], $\mu_2:\eta^1:\eta^2:\eta^1$ (Scheme S1c) [15,26–28] and $\mu_4:\eta^3:\eta^2:\eta^1$ (Scheme S1d) [29], but its analog, 3-ethoxy-2-hydroxybenzaldehyde (*Hehbd*), has just been reported of two coordination modes which are $\mu_1:\eta^1:\eta^1$ (Scheme 1b) [30–32] and $\mu_2:\eta^1:\eta^2:\eta^1$ (Scheme 1c) [15]. Herein, we want to study the coordination mode of *Hehbd* and construct new heterometallic coordination polymers. In our previous works, we have reported a number of heterometallic Co^{II} or $\text{Ni}^{\text{II}}/\text{M}$ ($\text{M}=\text{Li}^+$, Na^+ , K^+) clusters or coordination polymers [13–17]. In this paper, we report one new heterometallic 1-D chain $[\text{ZnNa}(\text{ehbd})_2(\text{N}_3)_n]_n$ (**1**) and one novel heterometallic $\text{Cu}^{\text{II}}/\text{Na}^{\text{I}}$ pentanuclear 2-D layer $[\text{Cu}_3\text{Na}_2(\text{ehbd})_2(\text{N}_3)_6]_n$ (**2**) which were synthesized at room temperature.

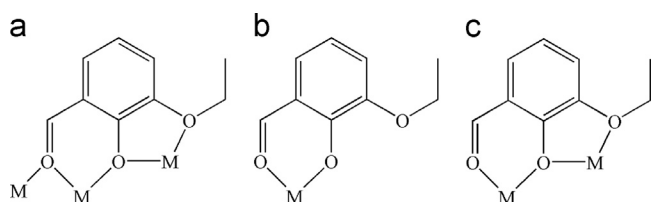
2. Experiment

2.1. Material and physical measurements

All chemicals were commercially available and used as received without further purification. Elemental analyses (CHN) were performed using an Elemental PE 2400 series II elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrophotometer. UV–vis spectra were recorded in the range 200–550 nm on a UV-2450 spectrophotometer.

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Scheme 1. Coordination modes of *ehbd* ligand.

Thermal analyses were performed in a nitrogen atmosphere at temperature in the range of 25–800 °C with a heating rate of 10 °C/min on a Mettler-Toledo TGA/SDTA851e thermobalance. The crystal structures were determined by single-crystal X-ray diffraction, using the SHELXL crystallographic software for molecular structures. Luminescence spectra were performed on a Hitachi F-4600 fluorescence spectrophotometer at room temperature. Magnetization measurements were carried out with a Quantum Design MPMS-XL7 SQUID to 5 T for **2**.

2.2. Synthesis

2.2.1. $[\text{ZnNa}(\text{ehbd})_2\text{N}_3]_n$ (**1**)

A mixture of $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (0.165 g, 0.75 mmol), *Hehbd* (0.125 g, 0.75 mmol), NaN_3 (0.0973 g, 1.5 mmol) and acetonitrile (10 mL) was stirred for 30 min at room temperature, then kept at room temperature. Yellow block crystals of **1** were obtained after 3 days. Yellow crystals of **1** were collected by filtration, washed with acetonitrile and dried in air. Phase pure crystals of **1** were obtained by manual separation (yield: 0.137 g, ca. 79.30% based on *Hehbd* ligand). *Anal. Calc.* for **1**: $\text{C}_{18}\text{H}_{18}\text{ZnN}_3\text{NaO}_6$ ($M_r=460.73$), *Calc.*: C, 46.88; H, 3.91; N, 9.11; Found: C, 46.76%; H, 3.97%; N, 9.18%. IR data for **1** (KBr, cm^{-1}): 3398 (w), 2076 (s), 1625 (s), 1538 (w), 1437 (m), 1335 (w), 1201 (s), 1099 (w), 897 (w), 742 (m).

2.2.2. $[\text{Cu}_3\text{Na}_2(\text{ehbd})_2(\text{N}_3)_6]_n$ (**2**)

Complex **2** can be prepared in a similar way to **1**, except that $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ was replaced by $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Black crystals of **2** were collected by filtration, washed with acetonitrile and dried in air. Phase pure crystals of **2** were obtained by manual separation (Yield: 0.124 g, ca. 60.7% based on Cu ion). *Anal. Calc.* for **2**: $\text{C}_{18}\text{H}_{18}\text{Cu}_3\text{N}_6\text{Na}_2\text{O}_6$ ($M_r=819.13$), *Calc.*: C, 26.43; H, 1.96; N, 30.84. Found: C, 26.39%; H, 2.01%; N, 30.89%. IR data for **2** (KBr, cm^{-1}): 3430 (m), 2930 (w), 2067 (s), 1600 (s), 1442 (w), 1332 (w), 1216 (m), 1090 (w), 890 (w), 747 (w).

Caution: Perchlorate salts and azide salts are potentially explosive and should be handled in small quantities and with great caution.

2.3. Crystal structure determination

Two diffraction data were collected on an Agilent G8910A CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å), using the ω - θ scan mode in the ranges $3.01^\circ \leq \theta \leq 25.01^\circ$ (**1**) and $3.63^\circ \leq \theta \leq 25.09^\circ$ (**2**). Raw frame data were integrated with the SAINT program. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [33]. An empirical absorption correction was applied with the program SADABS [33]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined as riding. Calculations and graphics were performed with SHELXTL [33]. The crystallographic details are provided in Table 1. Selected bond distances and angles for **1** and **2** are listed in Tables 2 and 3. Crystallographic data for the structural analysis have been deposited with the

Table 1
Crystallographic data for complexes **1** and **2**.

Complexes	1	2
Formula	$\text{C}_{18}\text{H}_{18}\text{N}_3\text{ZnNaO}_6$	$\text{C}_{18}\text{H}_{16}\text{N}_6\text{Cu}_3\text{Na}_2\text{O}_6$
Formula mass	460.73	817.12
Crystal size (mm)	$0.26 \times 0.18 \times 0.16$	$0.38 \times 0.34 \times 0.32$
Crystal system	Orthorhombic	triclinic
Space group	<i>Pbca</i>	<i>Pt</i>
<i>a</i> (Å)	11.234 (1)	9.198(2)
<i>b</i> (Å)	18.457 (1)	9.390(2)
<i>c</i> (Å)	19.130 (1)	10.640(2)
α (°)	90.00	64.87(2)
β (°)	90.00	69.44(2)
γ (°)	90.00	65.63(2)
<i>V</i> (Å ³)	3966.6 (2)	740.4(3)
<i>F</i> (000)	1888	407
<i>Z</i>	8	1
<i>D_c</i> (g cm ⁻³)	1.5429	1.833
μ (mm ⁻¹)	1.300	2.233
θ range (°)	3.01–25.01°	3.63–25.09
Ref. meas./indep.	10770, 3493	4223, 2596
Obs. ref. [$I > 2\sigma(I)$]	2656	1322
<i>R_{int}</i>	0.0271	0.0787
<i>R₁</i> [$I \geq 2\sigma(I)$] ^a	0.0382	0.0896
wR_2 (all data) ^b	0.0903	0.2453
Goof	1.040	1.007
$\Delta\rho$ (max, min) (e Å ⁻³)	0.5298, –0.6013	1.088, –0.878

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w |F_o^2|]^2$.

Table 2

Metal–ligand bond lengths and bond angles (°) of complex **1**.

N1–N2	1.118(4)	O3–Na1 ⁱⁱ	2.406(2)
N1–Zn1	1.937(3)	O4–Zn1	1.955(2)
N2–N3	1.128(5)	O6–Zn1	2.135(2)
Na1–O4	2.271(2)	O6–Na1 ⁱⁱ	2.408(2)
Na1–O1 ⁱ	2.272(2)	O1–Zn1	1.957(2)
Na1–O3 ⁱ	2.406(2)	O1–Na1 ⁱⁱ	2.272(2)
Na1–O5	2.407(2)	O2–Zn1	2.145(2)
Na1–O6 ⁱ	2.408(2)	Na1–O2	2.508(3)
O4–Na1–O1 ⁱ	163.15(9)	N1–N2–N3	171.7(5)
O4–Na1–O3 ⁱ	119.78(8)	Zn1–O6–Na1 ⁱⁱ	95.54(9)
O1 ⁱ –Na1–O3 ⁱ	67.45(8)	N1–Zn1–O4	117.71(14)
O4–Na1–O5	67.86(7)	N1–Zn1–O1	119.92(14)
O1 ⁱ –Na1–O5	125.95(9)	O4–Zn1–O1	122.36(9)
O3 ⁱ –Na1–O5	110.02(8)	N1–Zn1–O6	96.07(14)
O4–Na1–O6 ⁱ	95.53(8)	O4–Zn1–O6	88.34(8)
O1 ⁱ –Na1–O6 ⁱ	72.35(8)	O1–Zn1–O6	84.88(8)
O3 ⁱ –Na1–O6 ⁱ	137.00(8)	N1–Zn1–O2	97.85(14)
O5–Na1–O6 ⁱ	105.44(9)	O4–Zn1–O2	86.01(8)
O4–Na1–O2	71.52(8)	O1–Zn1–O2	87.40(9)
O1 ⁱ –Na1–O2	95.40(8)	O6–Zn1–O2	166.05(9)
O3 ⁱ –Na1–O2	83.63(9)	Zn1–O1–Na1 ⁱⁱ	105.39(9)
O5–Na1–O2	138.66(8)	Zn1–O2–Na1	93.95(9)
O6 ⁱ –Na1–O2	85.59(9)	Zn1–O4–Na1	107.38(9)

Symmetry codes: (i) $x-1/2, y, -z+3/2$; (ii) $x+1/2, y, -z+3/2$.

Cambridge Crystallographic Data Center (CCDC reference numbers: 1000126–1000127).

3. Results and discussion

3.1. Structural description

3.1.1. $[\text{ZnNa}(\text{ehbd})_2\text{N}_3]_n$ (**1**)

Single-crystal X-ray diffraction analysis reveals that **1** belongs to the orthorhombic space group *Pbca*. Each Zn^{II} ion of the monomer is coordinated with four O atoms from two different *ehbd*[−] ligands and one N atom from N_3^- formed a coordination anion $[\text{Zn}(\text{ehbd})_2(\text{N}_3)]^-$ (Fig. 1a). Herein, the *ehbd*[−] ligand displays the $\mu_3:\eta^2:\eta^2:\eta^1$

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