

Synthesis, Crystal Structure and Properties of a Chiral 2D Zn(II) Coordination Polymer with Helical Chains

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A chiral two-dimensional (2D) coordination polymer $\{[\text{Zn}(\text{cmm})\text{(1,4-bbi)}]\text{-H}_2\text{O}\}_n$ (**1**) has been synthesized by a hydrothermal reaction of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ with 4-(carboxymethoxy)-2-methylbenzoic acid (H_2cmm) and 1,1'-(1,4-butanediyl)bis(imidazole) (1,4-bbi). It has been characterized by elemental analysis, X-ray crystallography, IR spectroscopy and thermogravimetry, and also by its fluorescence properties. The metal-organic layer of the complex is held together with its neighbors via C–H...O hydrogen bonds to give rise to a chiral three-dimensional supramolecular network.

Key words: Helical, Chiral, Supramolecule, Hydrogen Bonding, Luminescence, Zinc, Benzoate Ligands

Introduction

In recent years, more and more attention has been focused on the construction of polymeric frameworks by reactions of metal salts with organic ligands, due to their intriguing structures and interesting properties [1–5]. Among the reported studies, those with carboxylate ligands are especially interesting because they can adopt a variety of coordination modes resulting in diverse multidimensional architectures [6–9]. The use of rigid carboxylate ligands has been reported frequently, while we focus our attention on flexible carboxylate ligands [10–12]. The use of auxiliary ligands is also an effective method for the formation of coordination polymers [13]. The auxiliary ligands can satisfy and even mediate the coordination geometry of the metal center and consequently generate designed architectures [14, 15]. From this point of

view, we use 1,1'-(1,4-butanediyl)bis(imidazole) (1,4-bbi) as the auxiliary ligand. Another noteworthy point is that coordination polymers containing metal ions with a d^{10} configuration, such as Zn(II), Cd(II) and Hg(II), are potential materials for optical applications, such as fluorescence probes and nonlinear optical materials [16–19].

Helical and homochiral structures received much attention owing to their relation to helical arrays in DNA chains. This kind of complexes have practical implications in multidisciplinary areas, such as optical devices, biomimetic chemistry, asymmetric catalysis, and structural biology [20–23].

In this paper we report the synthesis, structure, thermogravimetric analysis (TGA), and photoluminescence properties of a two-dimensional metal-organic polymer $\{[\text{Zn}(\text{cmm})\text{(1,4-bbi)}]\text{-H}_2\text{O}\}_n$ (**1**) with 4-(carboxymethoxy)-2-methylbenzoate (cmm $^{2-}$) and 1,1'-(1,4-butanediyl)bis(imidazole) (1,4-bbi) ligands.

Experimental Section

Materials and measurements

All the reagents and solvents were commercially available at analytical grade and were used without further purification or with purification by standard methods prior to use. Elemental analyses for C, H and N were carried out on a Perkin-Elmer 240 elemental analyzer. The Fourier transform infrared (FT-IR) spectra were obtained in the range of 4000–400 cm^{-1} from KBr pellets on a Bruker VECTOR 22 spectrometer. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer. Thermogravimetric measurements were carried out from r.t. to 700 °C on crystalline samples in a nitrogen stream using a SDT 2960 thermal analyzer at a heating rate of 20 °C min^{-1} .

Synthesis of 4-(carboxymethoxy)-2-methylbenzoic acid

The mixture of chloroacetic acid (1.290 g, 13.65 mmol) and 4-hydroxy-3-methylbenzoic acid (1.976 g, 13 mmol) in ethanol (10 mL) and NaOH (2.527 g, 63.18 mmol) in H_2O (40 mL) was refluxed at 100 °C for 12 h and then filtered after cooling to ambient temperature. A large amount of a colorless precipitate was obtained upon adding 1 M hydrochloric acid to the solution to reach pH = 1 and collected by filtration, washed with water and acetone, and dried in an oven at 105 °C for 10 h (89% yield). M.p. > 300 °C. – $\text{C}_{10}\text{H}_{10}\text{O}_5$ (210.20): calcd. C 57.14, H

4.76; found C 57.09, H 4.71. — IR (KBr): $\nu = 3434(\text{m}), 2924(\text{s}), 1714(\text{vs}), 1607(\text{s}), 1576(\text{m}), 1231(\text{m}), 1155(\text{w}), 950(\text{w}), 918(\text{s}), 873(\text{m}), 773(\text{m}), 749(\text{s}), 615(\text{s}) \text{ cm}^{-1}$. — ^1H NMR ($\text{D}_6\text{]DMSO}$): $\delta = 7.81$ (d, H, benzene), 6.76 (m, 2H, benzene), 4.59 (s, 2H, methylene), 2.49 (s, 3H, methyl) ppm.

Preparation of $\{[\text{Zn}(\text{cmmB})(1,4-\text{bbi})]\text{-H}_2\text{O}\}_n$

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.05 mmol, 14.9 mg), 4-(carboxymethoxy)-2-methylbenzoic acid (H_2cmmB ; 0.05 mmol, 10.5 mg) and 1,4-bbi (0.05 mmol, 9.5 mg) in distilled water (4 mL) and ethanol (2 mL) was placed in a Teflon-lined stainless-steel vessel. The vessel was sealed and heated to 120 °C for 3 d, and then cooled to room temperature. Colorless block-shaped crystals of complex **1** were obtained. Yield: 70% (based on zinc). — $\text{C}_{20}\text{H}_{24}\text{ZnN}_4\text{O}_6$ (481.80): calcd. C 49.81, H 4.98, N 11.62; found C 49.77, H 4.96, N 11.58. — IR (KBr): $\nu = 3566(\text{m}), 3430(\text{m}), 3148(\text{w}), 3120(\text{m}), 2949(\text{m}), 1608(\text{vs}), 1370(\text{vs}), 1281(\text{m}), 1229(\text{s}), 1171(\text{s}), 1103(\text{s}), 939(\text{w}), 913(\text{w}), 818(\text{w}), 747(\text{m}), 710(\text{s}), 630(\text{m}) \text{ cm}^{-1}$.

X-Ray crystallography

Single-crystal X-ray diffraction analysis of complex **1** was carried out at room temperature on a Bruker SMART APEX CCD diffractometer and investigated with graphite-monochromatized $\text{MoK}\alpha$ radiation at room temperature using ω -scans. The structure was solved by Direct Methods, completed by difference Fourier maps and refined by

Table 1. Crystallographic data for the coordination polymer **1**.

| Compound | 1 |
|---|---|
| Empirical formula | $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_6\text{Zn}$ |
| Formula weight | 481.80 |
| Color, habit | colorless, block |
| Crystal size, mm ³ | 0.21 × 0.20 × 0.19 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| <i>a</i> , Å | 8.2832(4) |
| <i>b</i> , Å | 15.7072(10) |
| <i>c</i> , Å | 16.3589(9) |
| <i>V</i> , Å ³ | 2128.4(2) |
| <i>Z</i> | 4 |
| <i>D</i> _{calcd.} , g cm ⁻³ | 1.50 |
| Absorption coeff., mm ⁻¹ | 1.2 |
| <i>T</i> , K | 293(2) |
| <i>F</i> (000), e | 1000 |
| Reflections collected / independent / <i>R</i> _{int} | 5319 / 3665 / 0.0303 |
| Independent reflections | |
| <i>R</i> 1 / <i>wR</i> 2 [$I > 2\sigma(I)$] | 0.0604 / 0.1416 |
| <i>R</i> 1 / <i>wR</i> 2 (all refls.) | 0.0737 / 0.1509 |
| Goodness-of-fit (GOF) | 1.035 |
| <i>x</i> (Flack) | -0.0313(17) |
| Largest difference peak / hole, e Å ⁻³ | 0.49 / -0.24 |

Table 2. Selected bond lengths (Å) and bond angles (deg) for the coordination polymer **1**^a.

| | | | |
|---------------------|----------|-------------------|----------|
| Zn(1)—O(2) | 1.946(5) | Zn(1)—N(4)#2 | 1.998(5) |
| Zn(1)—O(5)#1 | 1.967(5) | Zn(1)—N(1) | 2.015(6) |
| O(2)—Zn(1)—O(5)#1 | 115.5(2) | O(2)—Zn(1)—N(1) | 118.3(2) |
| O(2)—Zn(1)—N(4)#2 | 113.9(2) | O(5)#1—Zn(1)—N(1) | 100.5(2) |
| O(5)#1—Zn(1)—N(4)#2 | 100.2(2) | N(4)#2—Zn(1)—N(1) | 106.1(2) |

^a Symmetry codes: #1 $-x - 1/2, -y + 1, z - 1/2$; #2 $-x + 3/2, -y + 1, z + 1/2$.

full-matrix least-squares techniques using SHELXS-97 and SHELXL-97, respectively [24, 25]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The hydrogen atoms were assigned common isotropic displacement factors and included in the final refinement by using geometrical constraints. Crystal data and further information on the structure determination are summarized in Table 1. Relevant bond lengths and bond angles are given in Table 2.

CCDC 865627 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Description of the crystal structure

The single-crystal X-ray structure analysis revealed that **1** crystallizes in the asymmetric orthorhombic space group $P2_12_12_1$, and consists of right-handed helical chains. The metal coordination and atom labeling is depicted in Fig. 1. In each unit, there are one Zn^{2+} dication, one cmmB²⁻ dianion, one 1,4-bbi ligand and one free water molecule. The Zn atom is four-coordinated with two O atoms and two N atoms to form a distorted tetrahedral coordination geometry, with two oxygen atoms from two cmmB²⁻ ligands and two nitrogen atoms from two 1,4-bbi ligands. The Zn—O bond lengths are 1.946(5) and 1.967(5) Å, while the Zn—N bond lengths are 1.998(5) and 2.015(6) Å. The cmmB²⁻ ligands are monodentate in coordination with the Zn cations, and the uncoordinated carboxylic oxygen atoms have only weak interactions with the Zn atoms ($\text{Zn1—O1} = 2.8416(62)$ Å).

As shown in Fig. 2, there are two kinds of helical chains in the layer. The anionic cmmB²⁻ ligands connect the zinc cation ions along the *c* axis to generate

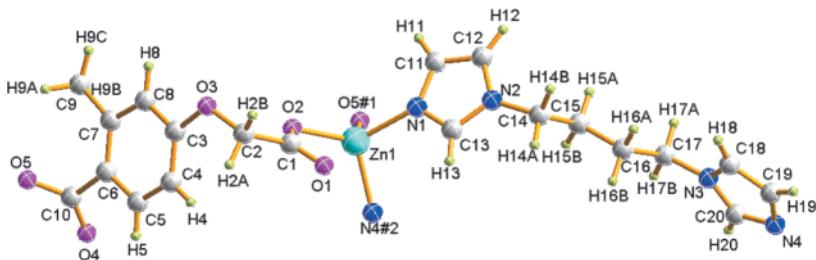


Fig. 1 (color online). Metal coordination and atom labeling in complex **1**. For symmetry operations see Table **2**.

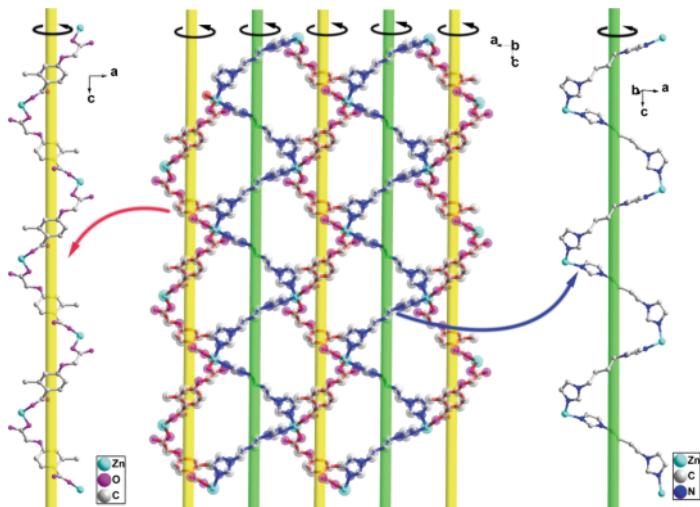


Fig. 2 (color online). A layer formed by right-handed helical chains.

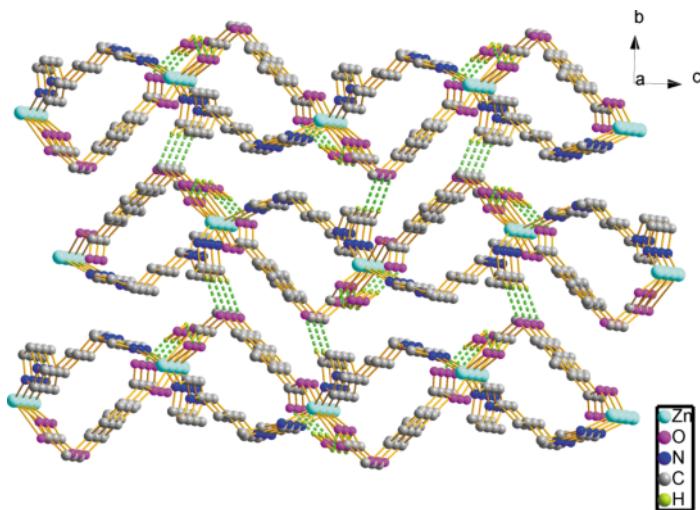


Fig. 3 (color online). 3D supramolecular framework formed by hydrogen bonding interactions.

a single right-handed helical chain. The 1,4-bbi ligands bridge the zinc ions of parallel helical chains in the *c* direction. The two kinds of helical chains have the same nearest Zn–Zn distance. The pitch of the helices

is 16.358 Å. The most salient structural feature of complex **1**, however, is the chiral coordination polymer assembled from achiral components in right-handed helices.

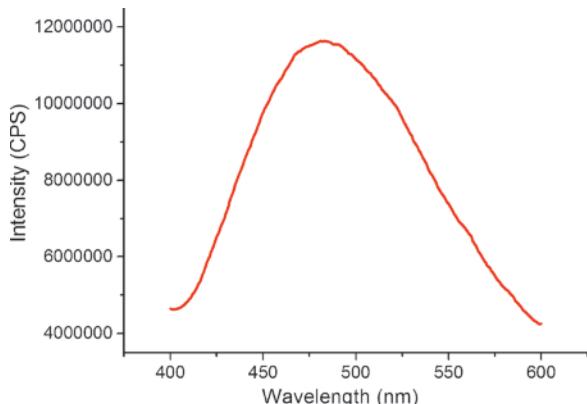


Fig. 4 (color online). Solid-state emission spectrum of complex **1** in the solid at r.t.

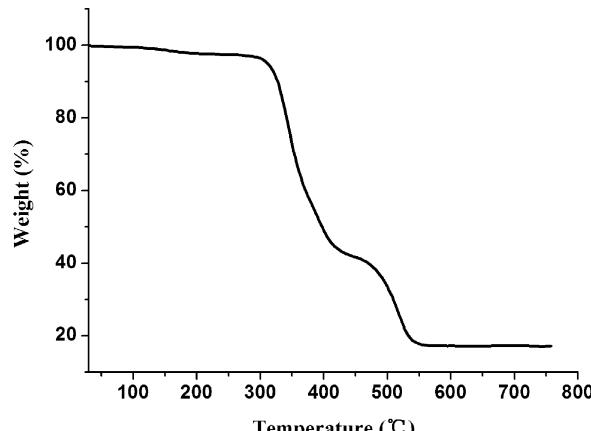


Fig. 5. Thermogravimetric analysis (TGA) of complex **1**.

As shown in Fig. 3, there are O–H…O hydrogen bonds between the O atoms from the uncoordinated water molecule (O6W) and the carboxylate group (O2, O4) with O6W…O2 and O6W…O4 distances of 2.975 and 2.792 Å, respectively. Hydrogen bonding interactions further consolidate the crystal structure, as in addition, C–H…O hydrogen bonds are also observed in the crystal. There is a C(19)–H(19)…O(3) hydrogen bond between the imidazole carbon atom C(19) of the 1,4-bbi ligand and the O(3) atom of the cmm²⁻ ligand of the adjacent layer. The C…O distance and the C–H…O angle are 3.310(8) Å and 161.002(4)°, respectively. It is well-known that hydrogen bonding is generally very important for generating supramolecular architectures [26]. With the help of these inter-chain hydrogen bonds, the adjacent layers give a 3D structure.

Photoluminescence properties of complex **1**

Luminescent compounds composed of d^{10} metal centers and organic ligands are of great interest because of their potential applications in the areas of chemical sensors and photochemistry [27]. Thus, we studied the photoluminescence properties of complex **1** and of the neutral acid H₂cmm^b in the solid state at room temperature. The complex shows luminescence with an emission maximum at 481 nm upon excitation at 318 nm (Fig. 4). The emission and excitation peaks of H₂cmm^b have their maxima at 348 and 318 nm, respectively. The emission maximum for complex **1** is therefore red-shifted

by 133 nm with respect to the band shown by the free ligand. The spectrum can tentatively be assigned to the intraligand $n-\pi^*$ or $\pi-\pi^*$ fluorescence emission [28].

Thermogravimetric analysis of complex **1**

Thermogravimetric analysis (TGA) was conducted to study the thermal stability of the title complex, which is an important aspect for metal-organic frameworks [29]. The TGA curve has three degradation steps in the range 29–694 °C. As depicted in Fig. 5, the first gradual weight loss of 3.5% occurs between 30 and 202 °C (calcd. 3.7%), corresponding to the loss of the uncoordinated water molecule per formula unit. Then, a plateau region is observed from 202 to 302 °C. On raising the temperature further, two consecutive decompositions take place in the temperature range of 302–587 °C. The calculated and observed overall losses correlate quite well (found 83%, calcd. 83.2%). Above 587 °C, no weight loss is observed, and the final residue obtained corresponds to the formation of zinc oxide (obsd: 17%, calcd. 16.8%).

Conclusion

In this paper, we have presented a chiral two-dimensional Zn(II) coordination polymer $\{[\text{Zn}(\text{cmm}^b)(1,4\text{-bbi})]\cdot\text{H}_2\text{O}\}_n$ assembled from cmm²⁻ and 1,4-bbi ligands under hydrothermal conditions. Our results indicate that the cmm²⁻

ligand has the potential to form chiral metal-organic frameworks when it reacts with metal ions, but also illustrate that hydrogen bonds have an influence on the formation of the supramolecular architecture.

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