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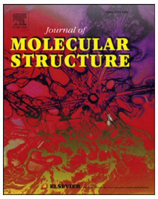

Structural variability, Hirshfeld surface analysis and properties of three Zn(II) coordination polymers based on flexible bis(thiabendazole) and aromatic dicarboxylate co-ligands

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ABSTRACT

Three zinc(II) coordination polymers (CPs), $\{[Zn(L)_{0.5}(tbta)]\cdot 0.5L\cdot 2.5H_2O\}_n$ (**1**), $\{[Zn(L)_{0.5}(mip)]\cdot H_2O\}_n$ (**2**) and $\{[Zn(L)_{0.5}(npht)(H_2O)]\cdot 0.5H_2O\}_n$ (**3**) (L = 1,4-bis(thiabendazole)butane, H_2tbta = tetrabromoterephthalic acid, H_2mip = 5-methylisophthalic acid, H_2npht = 3-nitrophthalic acid) have been hydrothermally synthesized and structurally characterized. Single-crystal X-ray diffraction analyses reveal that CP **1** shows a 2D honeycomb-like (6, 3) network. CP **2** displays a hybrid helical chain, and further assembled into a 2D supramolecular layer *via* weak C–H···O hydrogen bonding interactions, whereas CP **3** is a right-handed helical chain and finally extended into a 3D supramolecular structure by classical O–H···O hydrogen bonds and π–π stacking interactions. Further, the Hirshfeld surfaces, fingerprint plots, fluorescence properties and catalytic performances of three CPs for the degradation of methyl orange dye in a Fenton-like process have been investigated.

1. Introduction

Current state of research in the field of coordination polymers (CPs) has attracted considerable attention due to their enormous fascinating structures as well as their potential application in the fields of gas storage/separation, catalysis, luminescence, magnetism and sensors [1–3]. As it is known, their internal architectures decide their applications, so it is necessary to select appropriate metal centers, organic linkers, the metal-ligand ratio, temperature, pH and solvent to adjust their properties [4–6]. Among these factors, the organic ligands as connectors play the significant role in the construction of CPs through combination N-containing neutral ligands and organic acids [7]. Flexible bis(thiabendazole) ligands can show remarkable coordination ability and versatile conformations [8–13]. These ligands contains thiazolyl group, imidazole ring and a larger conjugated π system, capable of acting as π–π stacking interactions to diversify the frameworks of CPs and the –NH moieties can serve as electron acceptors in hydrogen bong interactions [14–18].

Aromatic carboxylate ligands are frequently used for the construction of CPs because of the diversity of the coordination modes and high structural stability, as well as they can act as hydrogen bond acceptors/donors for extension of coordination networks [19,20]. The significant procedure of analysis of their direct environment presents a considerable barrier in the understanding of structure and properties. Hirshfeld surface based tools represent a new method to solve this problem [21,22].

Herein three Zn^{II} CPs, namely, $\{[Zn(L)(tbta)]\cdot 2.5H_2O\}_n$ (**1**), $\{[Zn(L)_{0.5}(mip)]\cdot H_2O\}_n$ (**2**), and $\{[Zn(L)_{0.5}(npht)(H_2O)]\cdot 0.5H_2O\}_n$ (**3**) (L = 1,4-bis(thiabendazole)butane, H_2tbta = tetrabromoterephthalic acid, H_2mip = 5-methylisophthalic acid, H_2npht = 3-nitrophthalic acid) were obtained under hydrothermal conditions. The effect of aromatic carboxylate co-ligands on the assembly and structures of the Zn(II) CPs is discussed. The fluorescence properties and catalytic activities of CPs **1**–**3** were investigated.

2. Experimental

2.1. Materials and measurements

The ligand L was synthesized according to literature procedures [23]. All the other chemicals used for synthesis were of reagent

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grade and used without further purification. FT-IR spectra were obtained with an Avatar 360 (Nicolet) spectrophotometer using KBr pellets. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C automatic analyzer. Thermogravimetric analyses (TGA) were performed on a NETZSCH TG 209 thermal analyzer under flowing N_2 with a heating rate of 10 °C min^{-1}. X-ray powder diffraction (XRPD) patterns were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with Cu-Kα radiation ($\lambda = 1.5418$ Å). The fluorescence spectra of powdered solid samples were performed with a Hitachi F-7000 spectrophotometer at room temperature. The absorptivity value of methyl orange (MO) was recorded with a Puxi UV/Vis 1901 spectrophotometer.

2.2. Preparation of CPs

2.2.1. $\{[Zn(L)_{0.5}(tbta)]\cdot 0.5\ L\cdot 2.5H_2O\}_n$ (**1**)

A mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.1 mmol, 22 mg), L (0.1 mmol, 47 mg), H_2tbta (0.1 mmol, 48 mg), NaOH (0.2 mmol, 8 mg), and H_2O (12 mL) was placed in a Teflon-lined stainless steel autoclave. The mixture was sealed and heated at 140 °C for 3 days under autogenous pressure and cooled to room temperature at 10 °C/h, colorless block-shaped crystals of **1** were obtained with a yield of 69% (based on Zn). As shown in Table S1 (Supporting information). Anal. Calcd. for $C_{64}H_{50}Br_8N_{12}Zn_2O_{13}S_4$ (Mr = 2093.42): C 36.72, H 2.41, N 8.03%. Found: C 36.53, H 2.33, N 7.89%. IR (KBr, cm^{-1}): 3420 s, 1574 s, 1508 m, 1471 m, 1385 s, 1324 s, 1208 w, 1073 w, 845 m, 749 w.

2.2.2. $\{[Zn(L)_{0.5}(mip)]\cdot H_2O\}_n$ (**2**)

The synthetic procedure of **2** was similar to the synthesis of **1**, except that H_2mip (0.1 mmol, 18 mg) was used instead of H_2tbta. Colorless block-shaped crystals were obtained with a yield of 42% (based on Zn). Anal. Calcd. for $C_{21}H_{18}N_3ZnO_5S$ (Mr = 489.81): C 51.49, H 3.70, N 8.58%. Found: C 48.96, H 3.61, N 8.32%. IR (KBr, cm^{-1}): 3445 s, 1636 s, 1582 m, 1486 m, 1413 s, 1343 s, 1240 m, 1105 w, 941 w, 790w.

2.2.3. $\{[Zn(L)_{0.5}(npht)(H_2O)]\cdot 0.5H_2O\}_n$ (**3**)

The synthetic procedure of **3** was analogous to the synthesis of **1**, except that H_2npht (0.1 mmol, 21 mg) was used instead of H_2tbta. Colorless block-shaped crystals were collected with a yield of 48% (based on Zn). Anal. Calcd. for $C_{40}H_{32}N_8Zn_2O_{15}S_2$ (Mr = 1059.60): C 45.34, H 3.04, N 10.57%. Found: C 43.2, H 2.89, N 10.40%. IR (KBr, cm^{-1}): 3404 s, 1600 s, 1518 s, 1455 s, 1363 w, 1306 m, 1152 w, 911 m, 745 m.

2.3. X-ray crystallography

The data of **1**–**3** were collected on a Bruker Smart CCD diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å) using ω scan mode at 293 (2) K. Absorption corrections were applied by using SADABS program [24]. The structures of CPs **1**–**3** were solved by direct methods and refined with full-matrix least-squares technique based on F^2 with SHELXTL software package [25]. All non-hydrogen atoms were refined anisotropically. The crystal data and structure refinements for **1**–**3** are listed in Table 1, and selected bond distances and angles for **1**–**3** are listed in Table S2 (Supporting information).

Table 1
Crystal and refinement data for **1**–**3**.

	1	**2**	**3**
Formula	$C_{64}H_{50}Br_8N_{12}Zn_2O_{13}S_4$	$C_{21}H_{18}N_3ZnO_5S$	$C_{40}H_{32}N_8Zn_2O_{15}S_2$
Formula weight	2093.42	489.81	1059.60
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2/c$	$C2/c$
a (Å)	9.1362 (14)	10.0808 (3)	15.1118 (13)
b (Å)	13.7880 (2)	11.0257 (5)	19.1940 (17)
c (Å)	15.3310 (2)	17.6067 (5)	14.9516 (13)
α (°)	108.594 (2)	90	90
β (°)	90.176 (2)	99.318 (4)	107.741 (10)
γ (°)	96.007 (2)	90	90
V (Å^3)	1819.1 (5)	1931.13 (12)	4130.6 (6)
Z	1	4	4
D_{calc} (mg/m^3)	1.911	1.685	1.704
μ (mm^{-1})	5.237	1.422	1.347
F (000)	1026	1004	2160
θ_{max} (°)	27.51	26.37	27.49
R_{int}	0.0493	0.0872	0.0412
GOF	1.011	1.047	1.023
R_1 ($I > 2\sigma(I)$)	0.0491	0.0943	0.0410
wR_2 (all data)	0.0806	0.2398	0.0915
$\Delta\rho$max, eÅ^{-3}	0.516	1.843	0.423
$\Delta\rho$min, eÅ^{-3}	−0.497	0.855	0.574

2.4. Catalysis experiments

The catalytic reactions were tested using methyl orange (MO) as a model compound and the process was performed as follows: 0.01 mmol powder of CPs **1** (**2** or **3**) and 0.04 mmol of sodium persulfate were mixed together with 100 mL of MO solution (concentration 10.0 mg/L). The solution was kept continuously stirring with a magnetic stirrer, the temperature was controlled about 40 °C and the pH value was adjusted to 5.0 with 0.01 mol/L H_2SO_4. At given time intervals, 3.0 mL of the suspension was taken out and centrifuged to remove the residual catalyst, then measured for absorbance at 506 nm using Puxi UV/Vis 1901 spectrophotometer. The procedure was repeated in the absence of any catalyst as control experiments. The degradation efficiency (%D) is defined as:

$$\%D = (1 - C_t/C_0) \times 100\% \tag{1}$$

where C_0 (mg/L) is the initial concentration of MO, and C_t (mg/L) is its concentration at reaction time t (min).

3. Results and discussion

3.1. Crystal structure of $\{[Zn(L)_{0.5}(tbta)]\cdot 0.5\ L\cdot 2.5H_2O\}_n$ (**1**)

CP **1** crystallizes in a triclinic system with $P\bar{1}$ space group. The asymmetric unit of **1** consists of one Zn(II) center, a half coordinated L ligand, one $tbta^{2-}$ ligand, two and a half lattice water molecules and a half solvated L ligands. As shown in Fig. 1a, the Zn(II) center sits in a distorted octahedral geometry with the ZnO_4N_2 coordination environment defined by four oxygen atoms (O1, O2, O3, O4) from two different $tbta^{2-}$ ligands and two nitrogen atoms (N1, N2) from one L ligand. The Zn–O bond distances are in the range of 2.053 (4) Å and 2.423(4) Å, and the Zn–N bond lengths are 2.059(4)/2.090(4) Å, which are well matched to those observed in similar complexes [26].

Each independent L ligand adopts *trans*-conformation with two benzimidazole rings being in parallel fashion, in which the Zn···Zn distance is 12.116(16) Å. The carboxylate groups of $tbta^{2-}$ ligands coordinate to two Zn(II) ions in a (κ^1-κ^1)-(κ^1-κ^1)-μ_2 coordination mode. Each $tbta^{2-}$ ligand connects the adjacent zinc ions to form a 1D $[Zn(tbta)]_n$ zigzag chain, spanning Zn···Zn internuclear distances of 10.855(13) and 10.911(14) Å. The $[Zn(tbta)]_n$ chains are further linked by L ligand into a 2D (6, 3) grid (Fig. 1b), in which all Zn atoms can be considered as a 3-connected nodes, the L and $tbta^{2-}$ ligands can be regarded as linkers. In addition, intermolecular O–H···O (O2W–H2C···O1WD: 2.651(10) Å, 167(14)°; O2W–H2D···O4E: 3.150(9) Å, 147(9)°; symmetry code D: $-x+2$, $-y+1$, $-z+1$; E: $-x+1$, $-y+1$, $-z+1$) and O–H···N