Hydrothermal Synthesis, Crystal Structure and Properties of a 1D Metal-Organic Coordination Polymer $\{[Zn_2(2,2',3,3'\text{-odpa})(py)_3(H_2O)]\cdot H_2O\}_n$

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Hydrothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ with 2,2′,3,3′-oxydiphthalic acid (H_4odpa) and pyridine (py) at 120 °C yielded a one-dimensional metal-organic coordination polymer $\{[Zn_2(2,2',3,3'\text{-odpa})(py)_3(H_2O)]\cdot H_2O\}_n$ (**1**), which is further connected together through hydrogen bonds, $\pi\cdots\pi$ and $C-H\cdots\pi$ interactions to give a three-dimensional supramolecular network. The thermal stability of complex **1** was studied by thermal gravimetric (TG) and differential thermal analyses (DTA). Compound **1** exhibits photoluminescence with an emission maximum at *ca.* 430 nm upon excitation at 350 nm.

Key words: 2,2′,3,3′-Oxydiphthalic Acid, Coordination Polymer, Crystal Structure, Photoluminescence

Introduction

In recent years, the design and construction of multidimensional supramolecular solid-state architectures have attracted considerable attention in crystal engineering and supramolecular chemistry [1 – 4]. The self-assembly of multidentate organic ligands and metal ions has resulted in many coordination polymeric frameworks, whose structures are influenced by the subtle interplay of many factors such as geometric preference of metal ions, sizes and shapes of organic building blocks, templates, and solvent systems. The selection or design of suitable ligands containing certain features like flexibility or versatile binding modes is crucial to the construction of metal-organic coordination polymers. Moreover, the combination of both $\pi\cdots\pi$ interactions and hydrogen bonding has proved to be particularly useful for the assembly of polymeric structures [1 – 6]. The usual strategy which leads to higher dimensional complexes is to employ appropriate multidentate bridging ligands capable of binding metal ions by strong covalent or ionic interactions or of establishing supramolecular contacts by hydrogen bonding or stacking forces. The most widely used organic bridging ligands for coordination polymers are organic aromatic ligands containing two or more carboxylate groups separated by various spacers, rigid or flexible, from which a rich variety of one-, two- and three-dimensional metal-organic polymeric architectures have been constructed [7 – 14]. Several novel metal-organic coordination polymers assembled from 2,2′,3,3′-oxydiphthalic acid (H_4odpa) have been reported in previous papers [15, 16]. Herein a new one-dimensional coordination polymer $\{[Zn_2(2,2',3,3'\text{-odpa})(py)_3(H_2O)]\cdot H_2O\}_n$ (**1**) prepared from H_4odpa is described.

Experimental Section

Materials and measurements

2,2′,3,3′-Oxydiphthalic dianhydride (2,2′,3,3′-odpda) was synthesized according to the literature [17]. 2,2′,3,3′-H_4odpa was obtained through the hydrolysis of 2,2′,3,3′-odpda in the presence of HCl at reflux temperature in water. All other starting materials were of reagent quality obtained from commercial sources and used without further purification. Elemental analyses were carried out on an Elementar Vario EL III analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000 ∼ 400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. Thermogravimetric measurements were carried out from r. t. to 800 °C on crystalline samples in a nitrogen stream using a Seiko Exstar6000 TG/DTA6300 apparatus at a heating rate of 10 °C min^{-1}.

Preparation of the complex $\{[Zn_2(2,2',3,3'\text{-odpa})(py)_3(H_2O)]\cdot H_2O\}_n$ (1)

Colorless needle-shaped crystals of compounds **1** were synthesized hydro(solvo)thermally in a 23-mL Teflon-lined

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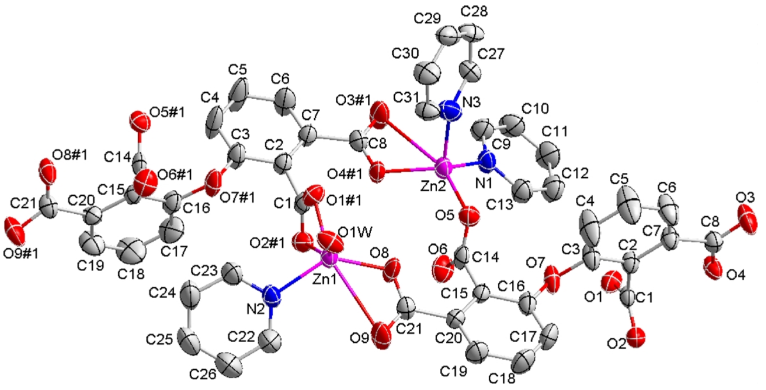

Fig. 1. ORTEP drawing of a structural unit of the title complex and crystallographic numbering scheme adopted (H atoms omitted for clarity).

Table 1. Crystal data, data collection parameters and details of the structure refinement.

Empirical formula	$C_{31}H_{25}N_3O_{11}Zn_2$
Formula weight	746.28
Color, habit	colorless, bar
Crystal size, mm^3	0.18 × 0.16 × 0.15
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	14.117(3)
b, Å	15.223(3)
c, Å	19.919(3)
β, deg	133.661(9)
Volume, Å^3	3096.8(10)
Z	4
Temperature, K	296(2)
Density (calcd.), g cm^{-3}	1.60
Absorption coeff., mm^{-1}	1.6
$F(000)$, e	1520
Radiation; wavelength, Å	MoK_α; 0.71073
Reflections collected / independent / R_{int}	15112 / 5438 / 0.056
Reflections with [$I \geq 2\,\sigma(I)$]	4234
Parameters refined	424
Final $R1$ / $wR2$ [$I \geq 2\,\sigma(I)$]	0.0343 / 0.0798
Final $R1$ / $wR2$ (all data)	0.0457 / 0.0824
Goodness of fit (GoF)	0.933
Final diff. peaks (max/min), eÅ^{-3}	+0.53 / −0.41

autoclave by heating a mixture of 0.1 mmol 2,2′,3,3′-H_4odpa, 0.3 mmol py, 0.2 mmol $Zn(NO_3)_2\cdot 6H_2O$ and 0.4 mmol NaOH at 120 °C in 8 mL of water and 2 mL of ethanol for 2 d. Colorless crystals of **1** were obtained after the solution was cooled to r. t. Yield: 70 %. – $Zn_2C_{31}H_{25}N_3O_{11}$ (746.28): calcd. C 49.85, H 3.38, N 5.63; found C 49.35, H 3.41, N 5.52. – IR (KBr, cm^{-1}): ν = 3408 (s), 2975 (w), 2927 (w), 1613 (s), 1605 (s), 1472 (vs), 1373 (s), 1241 (vs), 1071 (m), 820 (m), 767 (m), 640 (m), 488 (w).

X-Ray crystallographic study

A suitable single crystal of the title compound was mounted in random orientation on a glass fiber. Diffraction data were collected on a Bruker SMART APEX CCD diffractometer with MoK_α radiation using an ω scan mode in the range of $1.95 \leq \theta \leq 25.00°$. The structure was solved by Direct Methods and difference Fourier maps with SHELXS-97 [18], and refined by full-matrix least-squares techniques using SHELXTL-97 [19]. 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. Crystal data, data collection parameters and details of the structure refinement are given in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths (Å) and angles (deg) for the title complex[a].

Zn(1)–O(8)$^{\#1}$	1.933(2)	Zn(1)–O(1)	1.981(2)
Zn(1)–O(1W)	2.019(2)	Zn(1)–N(2)	2.033(2)
Zn(1)–O(9)	2.773(2)	Zn(1)–O(2)	2.544(2)
Zn(2)–O(5)$^{\#1}$	1.938(2)	Zn(2)–O(3)	2.834(2)
Zn(2)–N(1)	2.021(2)	Zn(2)–N(3)	2.057(3)
Zn(2)–O(4)	1.9328(18)		
O(8)$^{\#1}$–Zn(1)–O(1)	106.89(8)	O(8)$^{\#1}$–Zn(1)–O(1W)	108.21(9)
O(1)–Zn(1)–O(1W)	97.66(8)	O(8)$^{\#1}$–Zn(1)–N(2)	133.32(10)
O(1)–Zn(1)–N(2)	109.78(9)	O(1W)–Zn(1)–N(2)	94.56(9)
O(4)–Zn(2)–O(5)$^{\#1}$	110.81(8)	O(4)–Zn(2)–N(1)	127.79(9)
O(5)$^{\#1}$–Zn(2)–N(1)	105.64(9)	O(4)–Zn(2)–N(3)	98.51(10)
O(5)$^{\#1}$–Zn(2)–N(3)	103.03(10)	N(1)–Zn(2)–N(3)	108.33(10)

[a] Symmetry code: $^{\#1}$ $x, -y+3/2, z-1/2$.

CCDC 760235 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 structure

The title compound $\{[Zn_2(2,2',3,3'\text{-odpa})(py)_3(H_2O)]\cdot H_2O\}_n$ (**1**) was prepared hydrothermally. X-Ray analysis has revealed that the asymmetric unit contains two crystallographically nonequivalent Zn

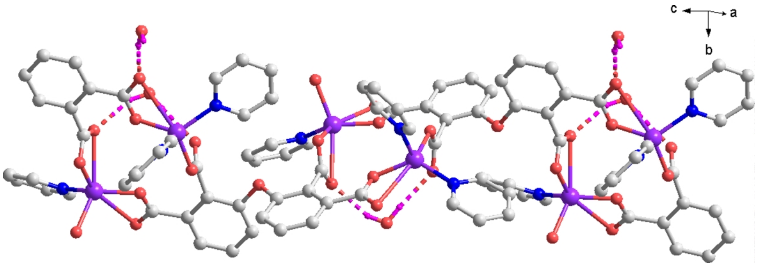

Fig. 2. A view of the one-dimensional chain structure of the title complex as seen along the crystallographic *c* axis.

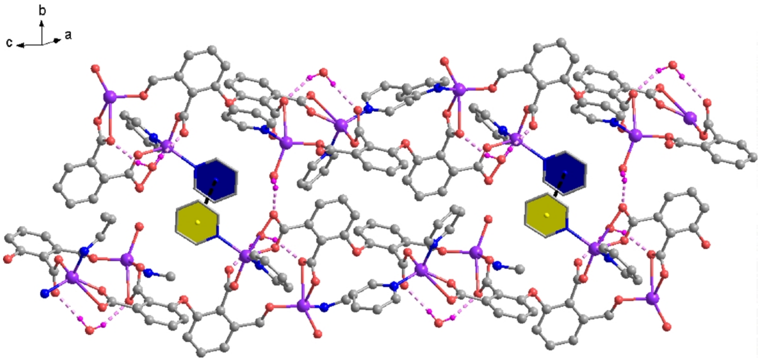

Fig. 3. Hydrogen bonds and $\pi\cdots\pi$ stacking interactions in the crystal of the title complex.

atoms (Zn1 and Zn2), one 2,2′,3,3′-odpa^{4-} anion, three neutral pyridine molecules, and one coordinated and one solvate water molecule. As shown in Fig. 1, the Zn1 center is coordinated by one 2-COO$^-$ in a bidentate fashion (O1 and O2), one 3-COO$^-$ of the neighboring ligand molecule in a monodentate fashion (O8), one nitrogen atom (N2) of a py molecule, and one oxygen atom of a water molecule. The Zn1–O9 distance of 2.773 Å of 3′-COO$^-$ suggests a non-negligible interaction. Thus, the Zn1 center has a distorted octahedral coordination geometry. The Zn2 atom is four-coordinated by one oxygen atom (O4) of 3-COO$^-$ and one oxygen atom (O5) of 2′-COO$^-$ of the neighboring ligand molecule, and two nitrogen atoms (N1 and N3) of two pyridine molecules. However, the Zn2–O3 distance of 2.834 Å of 3-COO$^-$ also suggests a non-negligible additional interaction. Therefore, the Zn2 center has a distorted square-pyramidal geometry. All bond lengths are normal: the Zn–N bond lengths are ranging from 2.021(2) to 2.056(3) Å and the Zn–O bond lengths from 1.933(18) to 2.834(18) Å. The Zn1$\cdots$Zn2 separation is 5.186(10) Å. As to the 2,2′,3,3′-odpa ligand, the dihedral angle between two phenyl rings is 87.6°. The 2- and 2′-carboxylate groups are almost perpendicular to the planes of the corresponding phenyl rings, with dihedral angles of 87.1° and 81.3°, respectively, but the 3- and 3′-carboxylate groups have dihedral angles of 2.2° and 18.0° with the planes of the corresponding phenyl rings, respectively. A twist is also observed between 2- (2′)- and 3- (3′)-carboxylate groups in odpa, the dihedral angles being 89.2° (72.6°).

Table 3. Hydrogen bond lengths (Å) and bond angles (deg)[a].

D–H$\cdots$A	d(D–H)	d(H$\cdots$A)	d(D$\cdots$A)	∠(DHA)
O(1W)–H(1WA)$\cdots$O(9)$^{\#3}$	0.85	1.80	2.649(3)	172.3
O(1W)–H(1WB)$\cdots$O(3)$^{\#4}$	0.85	1.82	2.652(3)	167.7
O(2W)–H(2WA)$\cdots$O(2)$^{\#5}$	0.85	2.02	2.825(3)	157.9
O(2W)–H(2WB)$\cdots$O(6)$^{\#6}$	0.85	2.06	2.906(3)	175.2

[a] Symmetry transformations used to generate equivalent atoms: $^{\#3}$ $-x+2, y-1/2, -z+3/2$; $^{\#4}$ $-x+1, y-1/2, -z+1/2$; $^{\#5}$ $-x+1, -y+1, -z+1$; $^{\#6}$ $-x+1, y-1/2, -z+3/2$.

The 2,2′,3,3′-odpa^{4-} ligands are linked to the Zn(II) atoms to give a one-dimensional metal-organic chain running along the *c* axis, as shown in Fig. 2. The solvate H_2O molecules form weak hydrogen bonds [O(2W)$\cdots$O2#3 2.825(3) Å; O(2W)$\cdots$O6#4 2.906(3) Å] with the carboxylate oxygen atoms O2 of 2-COO$^-$ and O6 of 2′-COO$^-$ of the neighboring ligand molecule in the same chain. The coordinated H_2O molecules form stronger inter-chain hydrogen bonds [O(1W)$\cdots$O9#3 2.649(3) Å; O(1W)$\cdots$O3#4 2.652(3) Å] with the carboxylate oxygen atoms O3 of 3-COO$^-$ and O9 of 3′-COO$^-$ from two different 2,2′,3,3′-odpa^{4-} ligands of adjacent chains. Strong O–H$\cdots$O hydrogen bonds thus play an important role in

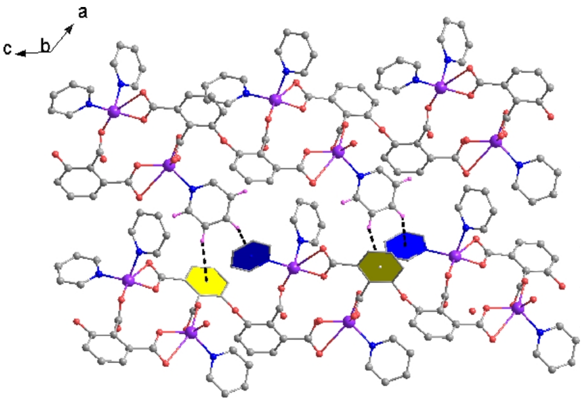

Fig. 4. The C–H$\cdots\pi$ stacking interactions in the title complex.

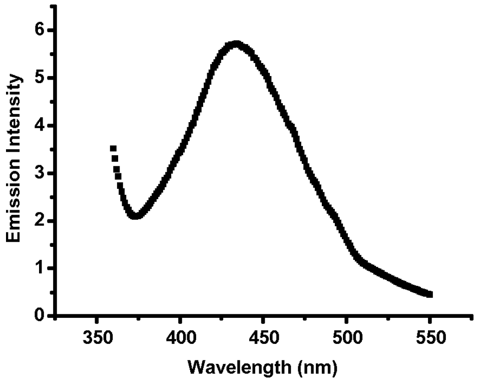

Fig. 5. Solid-state emission spectrum of **1** at room temperature.

stablizing the network structure and controlling the orientation of the 2,2′,3,3′-odpa^{4-} ligands. The hydrogen bonds are listed in Table 3.

At the same time, $\pi\cdots\pi$ stacking interactions between pyridine molecules of neighboring chains are also apparent in the title compound. These interactions only occur between N3-containing pyridine molecules coordinated to Zn2 atoms of neighboring chains, as shown in Fig. 3. The center-to-center distance between two parallel pyridine rings is 3.674(6) Å thus contributing to the stability of the supramolecular network [20].

In addition, the C25–H25 and C26–H26 bonds of N2-containing pyridine molecules coordinated to Zn1 atoms form C–H$\cdots\pi$ interactions (H25$\cdots\pi$ 3.120 Å; H26$\cdots\pi$ 3.067 Å) with N1-containing pyridine molecules coordinated to Zn2 atoms and phenyl rings containing 2-, 3-carboxylate groups of neighboring chains, as shown in Fig. 4. Thus the packing of **1** shows a three-dimensional supramolecular network *via*hydrogen bonds, $\pi\cdots\pi$ stacking interactions and C–H$\cdots\pi$ interactions.

Thermogravimetric analysis and photoluminescence properties

A thermogravimetric analysis (TGA) was conducted to determine the thermal stability of this complex, which is an important aspect for metal-organic frameworks. TGA was performed on crystalline samples of **1** in the range of 25 – 800 ℃. The results indicate that a weight loss of 5.0 % below 178 ℃ corresponds to the loss of one solvate and one coordinated water molecule per formula (calcd.: 4.8 %). The sample did not decompose any further below 278 ℃.

The emission spectrum of compound **1** in the solid state at r. t. is shown in Fig. 5. Photoluminescence with an emission maximum at *ca.* 430 nm occurs upon excitation at 350 nm. According to literature [21], these emission bands can be assigned to ligand-to-metal charge transfer (LMCT). Compound **1** may be an excellent candidate for blue-fluorescent materials.

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