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Hydrothermal Synthesis and Structural Characterization of a One-Dimensional Coordination Polymer $[Zn(Pydc)(Dppz)]_n$ (H_2Pydc = 2,6-Pyridinedicarboxylic Acid, Dppz = Dipyrido[3,2-a:2',3'-c]Phenazine)[1]

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Abstract—A new metal-organic coordination polymer $[Zn(Pydc)(Dppz)]_n$ (**I**) (H_2Pydc = 2,6-pyridinedicarboxylic acid, Dppz = dipyrido[3,2-a:2',3'-c]phenazine) was hydrothermally synthesized and characterized by elemental analysis, IR and X-ray single-crystal diffraction. The X-ray diffraction analysis reveals that **I** crystallizes in the monoclinic system, space group $P2_1/c$. The $Pydc^{2-}$ ligands adopt O,N,O'-tridentate chelating and monodentate bridging coordination mode to link two adjacent Zn^{2+} ions to form a one-dimensional (1D) zigzag chain. The adjacent chains are further linked through hydrogen bonds and π–π stacking interactions, forming a three-dimensional (3D) supramolecular framework. The unit cell parameters for **I**: $a = 7.332(3)$ Å, $b = 36.023(9)$ Å, $c = 7.8838(13)$ Å, $\beta = 105.65(3)^\circ$, $V = 2005.1(10)$ Å^3, $Z = 4$.

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INTRODUCTION

During the past two decades, the rational design and synthesis of new metal-organic coordination polymers (MOCPs) with infinite one-dimensional (1D) chains, two-dimensional (2D) grids, and three-dimensional (3D) network structures have attracted considerable attention in coordination chemistry not only because of their intriguing architectures and topologies, but also owing to their fascinating applications as functional materials in magnetism, gas absorption and separation, ion exchange, asymmetric catalysis, nonlinear optics, and so on [1–7]. Several approaches have previously been reported for constructing MOCPs, including the solvent evaporation method, interface diffusion method, hydro(solvo)thermal synthesis and ionothermal synthetic techniques, etc. Among them, the hydro(solvo)thermal technique has been widely used in synthesizing novel MOCPs owing to their products have high purity, good dispersion and easy to control, etc. [8–11]. Recently, many MOCPs have been obtained by selecting appropriate building blocks with heterocyclic carboxylic acids, such as pyridine, pyrazole, and imidazole carboxylic acids under hydro(solvo)thermal conditions [12–16]. Among them, 2,6-pyridinedicarboxylic acid is an important ligand for transition metal complexes due to the versatile bidentate, tridentate, or bridging coordination modes [17, 18]. In this paper, we report a new 1D zigzag coordination polymer, $[Zn(Pydc)(Dppz)_2]_n$ (**I**) (H_2Pydc = 2,6-pyridinedicarboxylic acid, Dppz = dipyrido[3,2-a:2',3'-c]phenazine), which has been prepared by the hydrothermal reactions of H_2Pydc ligand with $Zn(NO_3)_2 \cdot 6H_2O$ and Dppz ligand and characterized by elemental analysis, infrared spectroscopy (IR) and X-ray single-crystal diffraction.

EXPERIMENTAL

Materials and methods. The Dppz ligand was synthesized according to the literature method [19]; all other reagents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a PerkinElmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrometer.

Hydrothermal synthesis. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.148 g, 0.5 mmol), H_2Pydc (0.084 g, 0.5 mmol), Dppz (0.141 g, 0.5 mmol), NaOH (0.040 g, 1.0 mmol), and distilled water (10 mL) was in a 23 mL Teflon-lined stainless steel autoclave for 20 min in air. Then it was heated at 433 K for 5 days followed by cooling to room temperature at a rate of 5 K/h. The resulting colorless block crystals of **I** were isolated by filtration, washed with distilled water and dried in air (the yield is ~63%). Compound **I** is insoluble in water and common organic solvents, such as DMF, DMA,

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[1] The article is published in the original.

Table 1. Crystallographic parameters and summary of data collection for structure

Parameter	Value
Formula weight	512.77
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	7.332(3)
b, Å	36.023(9)
c, Å	7.8838(13)
β, deg	105.65(3)
V, Å^3	2005.1(10)
Z	4
ρ_{calcd}, mg cm^{-3}	1.699
Absorption coefficient, mm^{-1}	1.273
F(000)	1040
Crystal size, nm	0.37 × 0.37 × 0.29
θ Range, deg	2.26–26.00
Limiting indices h, k, l	$-8 \le h \ge 9$, $-42 \le k \ge 1$, $-9 \le l \ge 1$
Scan mode	ω-scan
Reflections collected	4542
Independent reflections (R_{int})	3541 (0.0553)
Reflections with $I > 2\sigma(I)$	1875
T, K	293(2)
Parameters	316
GOOF	1.069
Final R indices ($I > 2\sigma(I)$)*	$R_1 = 0.1003$, $wR_2 = 0.2421$
R indices (all data)	$R_1 = 0.2055$, $wR_2 = 0.3452$
Largest diff. peak and hole, e Å^{-3}	1.899 and −1.413

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

Table 2. Selected bond distances (Å) and angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Zn(1)–N(1)	1.979(10)	Zn(1)–O(3)	2.200(9)
Zn(1)–N(2)	2.055(11)	Zn(1)–O(4)$^{\#1}$	2.242(10)
Zn(1)–O(2)	2.096(9)	Zn(1)–N(3)	2.270(11)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)Zn(1)N(2)	171.9(4)	O(2)Zn(1)O(4)$^{\#1}$	95.5(4)
N(1)Zn(1)O(2)	80.5(4)	O(3)Zn(1)O(4)$^{\#1}$	92.8(4)
N(2)Zn(1)O(2)	94.0(4)	N(1)Zn(1)N(3)	91.7(4)
N(1)Zn(1)O(3)	70.5(3)	N(2)Zn(1)N(3)	81.8(4)
N(2)Zn(1)O(3)	114.6(4)	O(2)Zn(1)N(3)	84.1(4)
O(2)Zn(1)O(3)	150.8(4)	O(3)Zn(1)N(3)	93.9(4)
N(1)Zn(1)O(4)$^{\#1}$	101.1(4)	O(4)$^{\#1}$Zn(1)N(3)	167.0(4)
N(2)Zn(1)O(4)$^{\#1}$	85.3(4)		

* Symmetry codes: $^{\#1}$ x, $-y + 1/2$, $z + 1/2$.

DMSO, CH_3CN, methanol, ethanol, benzene, toluene, and acetone.

For $C_{25}H_{13}N_5O_4Zn$

anal. calcd., %: C, 58.56; H, 2.56; N, 13.66.

Found, %: C, 58.60; H, 2.52; N, 13.68.

IR spectrum (KBr, ν, cm^{-1}): 2924 w, 2360 m, 1601 v.s, 1355 v.s, 1276 m, 1074 m, 904 w, 817 m, 780 m, 760 m, 669 m.

X-ray crystal determination. Single-crystal X-ray diffraction measurements were carried out on a Bruker P4 diffractometer at 293(2) K temperature. The data collections were performed with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator using the ω scan mode. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [20]. All non-hydrogen atoms were treated anisotropically. Positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details for structural analyses are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2, π–π stacking parameters (Å) is listed in Table 3, hydrogen bonding geometric data is listed in Table 4. Supplementary material has been deposited with the Cambridge Crystallographic Data Cen-

Table 3. π–π Stacking parameters (Å) for **I***

Cg(I), Cg(J)	Cg(I)-Cg(J)	Cg(I)-Perp	Cg(J)-Perp	Slippage	Symmetry codes
Cg(7), Cg(7)	5.204(8)	3.259(6)	3.259(9)	4.058	$3 - x, -y, 1 - z$
Cg(7), Cg(9)	3.735(9)	3.225(6)	3.243(6)		$3 - x, -y, 1 - z$
Cg(8), C(9)	5.227(8)	3.217(5)	3.171(6)		$3 - x, -y, 1 - z$
Cg(9), Cg(7)	3.736(9)	3.244(6)	3.225(6)		$3 - x, -y, 1 - z$
Cg(9), C(8)	5.227(8)	3.171(6)	3.216(5)		$3 - x, -y, 1 - z$
Cg(9), Cg(9)	3.425(9)	3.240(6)	3.240(6)	1.111	$3 - x, -y, 1 - z$

* Cg–Cg is the distance between ring centroids; Cg(I)–Perp is the perpendicular distance of Cg(I) on ring J; Cg(J)-Perp is the perpendicular distance of Cg(J) on ring I; slippage is the distance between Cg(I) and perpendicular projection of Cg(J) on Ring I. Cg(4) is the centroid of the N(1)/C(2)/C(3)/C(4)/C(5)/C(6) plane, Cg(5) is the centroid of the N(2)/C(8)/C(9)/C(10)/C(11)/C(25) plane, Cg(6) is the centroid of the N(3)/C(23)/C(22)/C(21)/C(20)/C(24) plane, Cg(7) is the centroid of the N(4)/C(12)/C(19)/N(5)/C(18)/C(13) plane, Cg(8) is the centroid of the C(11)/C(12)/C(19)/C(20)/C(24)/C(25) plane, Cg(9) is the centroid of the C(13)/C(14)/C(15)/C(16)/C(17)/C(18) plane.

Table 4. Hydrogen bonding parameters in **I**

Contact D–H···A	Distance, Å			Angle D–H···A, deg	Symmetry operations for *A*
	D–H	H···A	D···A		
C(4)–H(4*A*)···O(3)	0.93	2.46	3.20(2)	136	$-1 + x, 1/2 - y, -1/2 + z$
C(8)–H(8*A*)···O(4)	0.93	2.34	2.920(17)	120	$x, 1/2 - y, 1/2 + z$

tre (no. 831889; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

X-ray structural analysis shows that **I** crystallizes in the monoclinic system, space group $P2_1/c$ with the asymmetric unit consisting of one Zn^{2+} ion, one Pydc ligand, and one Dppz ligand. The Zn^{2+} ion is six-coordinated by three oxygen atoms (O(1), O(2), O(4*A*)) and three nitrogen atoms (N(1), N(2), N(3)) from one chelating Dppz ligand and two different Pydc ligands, respectively (Fig. 1). The coordination geometry around the Zn^{2+} ion can be described as a distorted octahedron with Zn–O bond lengths ranging from 2.096(9) to 2.242(10) Å, Zn–N bond lengths ranging from 1.979(10) to 2.270(11) Å (Table 2). The Pydc ligands adopt O,N,O'-tridentate chelating and mono-

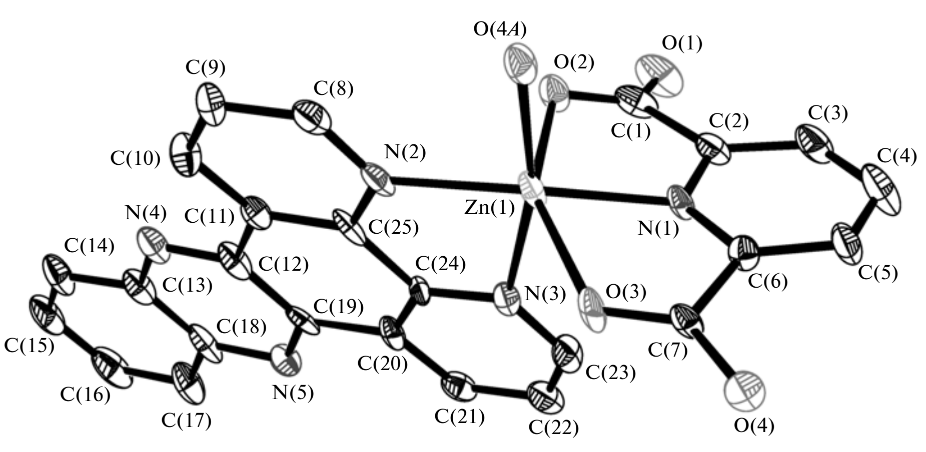

Fig. 1. Coordination environment of the Zn^{2+} ion in **I**.

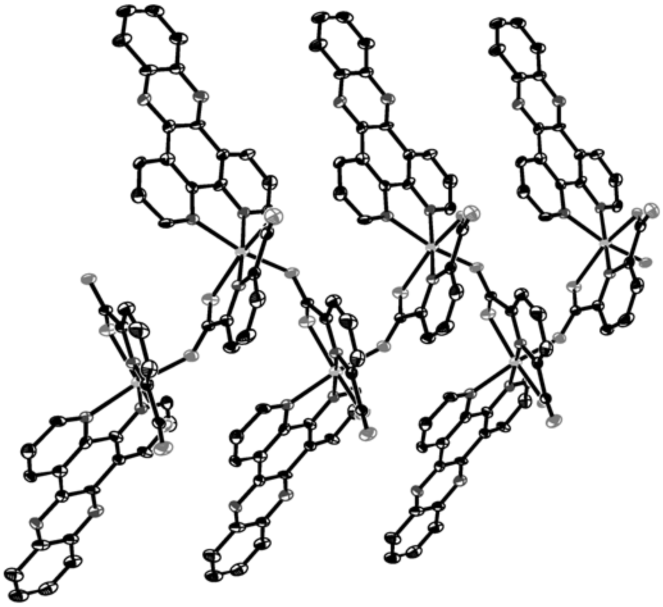

Fig. 2. Fragment of 1D zigzag chain structure in **I**.

dentate bridging coordination mode to link two adjacent Zn^{2+} ions to form a one-dimensional zigzag chain, in which the 2-carboxyl group bridges two adjacent Zn^{2+} ions in an *anti-anti* coordination mode with the Zn···Zn distances of 6.1223(24) Å. The Dppz ligands adopt bidentate chelation mode to connect one Zn^{2+} ion, which point away from the zigzag chain like wings to form a roof-like arrangement (Fig. 2). The conformation of the chain is severely puckered with the Zn···Zn···Zn angle between adjacent metal centers of 80.16(3)° and the minimum distance observed between two adjacent pyridine rings centroids is 4.106(9) Å. The lateral Dppz ligands from adjacent chains are further connected together by π–π stacking interactions [21]. The π–π stacking interactions are observed between pyridine rings and aromatic rings of the planar Dppz ligands with a perpendicular separation range from 3.171(6) to 4.125(6) Å, and a centroid-to-centroid distance range from 3.425(9) to 5.227(8) Å (Table 3). These values are typical of aromatic π–π stacking interactions [22]. In addition, there exist C–H···O intra- and intermolecular typical hydrogen bonds (Table 4). Adjacent chains are further linked *via* hydrogen bonds and π–π stacking interactions to construct a three-dimensional supramolecular network (Fig. 3), these weak interactions enhance the stability of the complex.

The IR spectrum of **I** illustrates that the characteristic bands of carboxyl groups at 1601 cm^{-1} for the asymmetric stretching and at 1355 cm^{-1} for symmetric stretching. $\Delta(\nu_{as} - \nu_s) = 1601-1355 = 246-200$ cm^{-1} demonstrates the monodentate of all the carboxylic group to the Zn(II) [23, 24]. The absence of strong characteristic peaks around 1700 cm^{-1} reveals that all carboxylic groups are completely deprotonated [25], which is consistent with the results of the X-ray analysis.

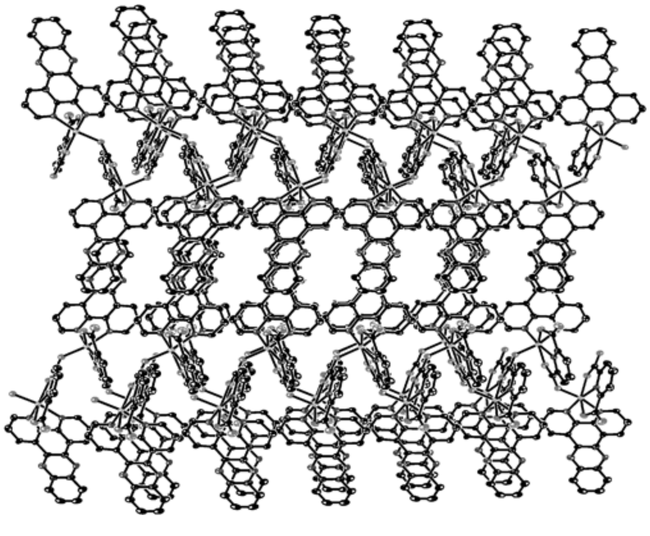

Fig. 3. 3D supramolecular framework of **I** viewed along the *x* axis.

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