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A New Complex Constructed by Zn(II) with Pydc and Bipy Ligands (H_2Pydc = 2,5-Pyridinedicarboxylic Acid, Bipy = 4,4'-Bipyridine)[1]

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Abstract—A new complex $[Zn_2(Pydc)_2(Bipy)(H_2O)_8]$ (**I**) (H_2Pydc = 2,5-Pyridinedicarboxylic Acid, Bipy = 4,4'-bipyridine) was hydrothermally synthesized and characterized by elemental analyses and single crystal X-ray diffraction. The X-ray diffraction analysis reveals that I is a discrete binuclear Zn(II) complex and the adjacent binuclear units are further connected together via the strong H-bonding interactions.

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INTRODUCTION

In recent years, the low-dimensional coordination polymers have received much attention owing to their intriguing structural features and potential application as functional materials different from those of 3D coordination polymers [1–6]. The hydro(solvo)thermal method has been a promising technique in synthesizing novel metal-organic frameworks [7–11]. Recently, building blocks with heterocyclic carboxylic acids, such as pyridine-, pyrazole-, and imidazole carboxylic acids have been used in the construction of coordination polymers [12–16]. Among them, 2,5-dipicolinate is a polydentate ligand having the coordination ability of both dicarboxylate and pyridyl ligands and is expected to produce new cluster topologies by virtue of its coordinative flexibility [17]. It is noted that Pydc has recently been used in the preparation of polymeric Ln(III)/Cu, Ag, and Zn mixed metal complexes [18–20]. With the intention of preparing Pydc-metal polymer, we choose the Bipy ligand that strongly favors bridging coordination, and a new complex $[Zn_2(Pydc)_2(Bipy)_2(H_2O)_8]$ (**I**) (H_2Pydc = 2,5-Pyridinedicarboxylic acid (2,5-dipicolinato), Bipy = 4,4'-Bipyridine) was successfully synthesized. In this paper, we reported its synthesis and crystal structure.

EXPERIMENTAL

All reagents and solvents employed were commercially available and used as received without further purification.

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), Bipy (0.067 g, 0.5 mmol), NaOH (0.04 g, 1 mmol), and H_2O (10 ml) was in a 23-ml teflon reactor for 20 min in air. Then it was heated at 160°C for five days followed by cooling to room temperature at a rate of 5°C/h. The resulting colorless block crystals of **I** were isolated. Compound **I** is insoluble in water and common organic solvents, such as DMF, DMSO, CH_3CN, benzene, toluene, methanol, ethanol, and acetone. The yield was 67%.

For $C_{17}H_{19}N_3O_8Zn$

anal. calcd, %:	C, 44.51;	H, 4.17;	N, 9.16.
Found, %:	C, 44.53;	H, 4.14;	N, 9.15.

X-Ray diffraction analysis. Crystallographic data of **I** were collected at room temperature (293(2) K) on a Bruker P4 diffractometer with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator using the scan mode. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL [21]. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. The crystallographic data and experimental details for structural analysis are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 606971; deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

[1] The article is published in the original.

Table 1. Summary crystallographic data for compound **I**

Parameter	Value
M	917.44
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a, Å	7.7685(9)
b, Å	8.2998(14)
c, Å	15.304(4)
a, deg	104.853(18)
β, deg	99.666(17)
γ, deg	90.768(12)
Volume, Å^3	938.6(3)
Z	2
ρ_{calcd}, g/cm^3	1.623
μ, mm	1.361
F(000)	472
Crystal size, mm	0.37 × 0.31 × 0.23
θ Range, deg	2.54–26.01
Reflections collected	4497
Independent reflections (R_{int})	3657 (0.0237)
Max, min transmission	0.7404, 0.6336
Goodness-of-fit on F^2	1.057
Number of refined parameters	270
Final R indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.0420$ $wR_2 = 0.1112$
R indices (all data)	$R_1 = 0.0533$ $wR_2 = 0.1215$
Largest diff. peak and hole, e Å^{-3}	0.571 and –0.633

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

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

Bond	d, Å	Bond	d, Å
Zn(1)–O(1)	2.107(3)	Zn(1)–O(1w)	2.137(3)
Zn(1)–O(2w)	2.062(3)	Zn(1)–O(3w)	2.127(3)
Zn(1)–N(2)	2.127(3)	Zn(1)–N(1)	2.158(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(2w)Zn(1)O(1)	175.22(11)	N(2)Zn(1)O(2w)	95.50(11)
N(2)Zn(1)O(1)	86.92(10)	O(2w)Zn(1)O(3w)	86.73(11)
O(1)Zn(1)O(3w)	97.35(11)	O(3w)Zn(1)N(2)	91.38(11)
O(2w)Zn(1)O(1w)	83.13(11)	O(1w)Zn(1)O(1)	92.62(12)
N(2)Zn(1)O(1w)	93.29(12)	O(3w)Zn(1)O(1w)	169.20(11)
N(1)Zn(1)O(2w)	100.82(10)	N(1)Zn(1)O(1)	77.11(10)
N(1)Zn(1)N(2)	163.18(11)	O(3w)Zn(1)N(1)	85.56(10)
O(1w)Zn(1)N(1)	92.67(11)		

RESULTS AND DISCUSSION

The X-ray structural analysis shows that **I** crystallizes in triclinic crystal system space group $P\bar{1}$, with an asymmetric unit of the unit cell consisting of one Zn center, one Pydc ligand, two halves of Bipy ligand, three coordination water molecules, and one lattice water molecule. The Zn center is octahedrally coordinated with four oxygen atoms from the carboxyl and three coordination water molecules in the equatorial plane (Zn(1)–O(1) 2.107(3), Zn(1)–O(1w) 2.137(3), Zn(1)–O(2w) 2.062(3), Zn(1)–O(3w) 2.127(3) Å), with two nitrogen atoms from Bipy and Pydc ligands in the axial positions (Zn(1)–N(1) 2.158(3), Zn(1)–N(2) 2.127(3) Å). The OZnO bond angles range from 77.11(10)° to 175.22(11)° (Fig. 1). The Pydc ligands coordinate in only one way, which is the bidentate (N, O) chelate mode to coordinate one Zn^{2+} ion.

The two Zn^{2+} ions were first chelated by two Pydc ligands and six coordination water molecules. Then they were connected by the Bipy ligand to form a centrosymmetric binuclear unit as shown in Fig. 2. Adjacent binuclear units were connected together by strong

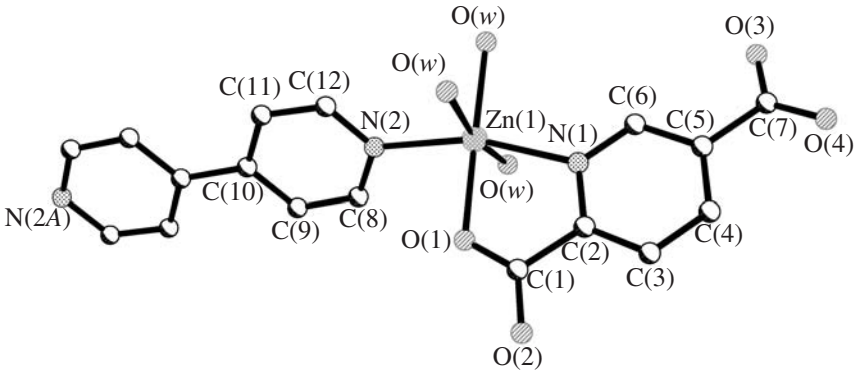

Fig. 1. Coordination environment of the Zn(II) center in **I**.

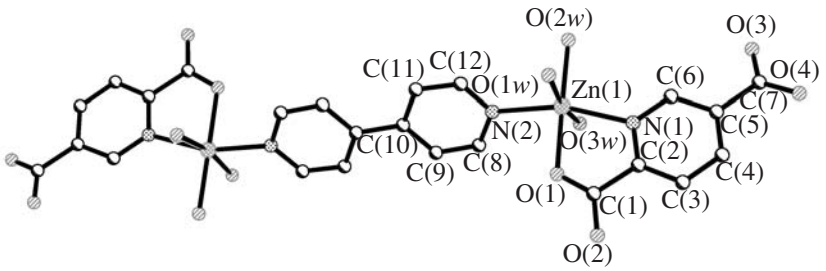

Fig. 2. Binuclear unit in **I**.

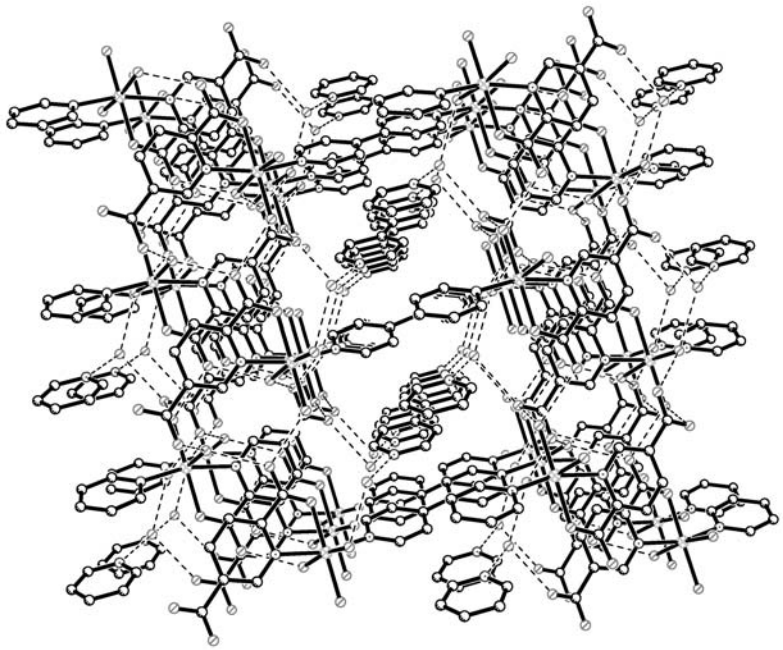

Fig. 3. View of the 3D structure of **I** along the *y* axis.

Table 3. Geometric parameters of hydrogen bonds in structure **I***

D–H···A bond	Distance, Å		The D–H···A angle, deg
	D–H	D···A	
O(3*w*)–H(3*wA*)···O(2)$^{\#1}$	0.82	2.720(2)	163
O(1*w*)–H(1*A*)···O(3)$^{\#2}$	0.82	2.894(2)	167
O(1*w*)–H(1*B*)···O(4*w*)	0.82	2.705(3)	168
O(4*w*)–H(4*wA*)···N(3)	0.82	2.775(2)	164
O(2*w*)–H(2*A*)···O(2)$^{\#3}$	0.82	2.707(3)	155
O(2*w*)–H(2*B*)···O(4)	0.82	2.742(3)	167
O(3*w*)–H(3*B*)···O(3)$^{\#4}$	0.82	2.789(3)	166
O(4*w*)–H(4*wB*)···O(4)$^{\#5}$	0.82	2.787(2)	170
C(9)-H(9*A*)···O(4*w*)$^{\#6}$	0.93	3.377(4)	171

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

hydrogen bonding interactions between the carboxylate groups of the Pydc ligands and the coordinated water molecules to construct a 3D structure (Table 3). The size of pores, which were formed by adjacent binuclear units, was about 7.8×11.3 Å^2. One lattice Bipy ligand and two lattice water molecules exist in every pore, which also had strong hydrogen bonding and enhanced the stability of the complex (Fig. 3).

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