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Synthesis and Crystal Structures of Two Zinc(II) Complexes with 4-Hydroxypyridine-2,6-Dicarboxylic Acid[1]

Y. F. Wang[a, *], L. L. Zang[b], and J. F. Liu[a]

[a]*College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, Henan, 471022 P.R. China*

[b]*Handan Fire Detachment, Hebei, Handan, 056000 P.R. China*

**e-mail: wangyf78@163.com*

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Abstract—Two new complexes $[Zn(Hpda)(Bth\text{-}6)]_{2n}$ (**I**) and $[Zn(Hpda)_2] \cdot 2(H\text{-}Bpe)$ (**II**) ($HpdaH_2$ = 4-hydroxypyridine-2,6-dicarboxylic acid, Bth-6 = 1,6-bis(1,2,4-triazol-1-yl)hexane, Bpe = 1,2-bi(4-pyridyl)ethene) have been synthesized and characterized structurally. Their X-ray crystal structures show that the two complexes belong to a monoclinic system; space group $P2_1/n$ with $a = 11.9328(12)$, $b = 20.975(2)$, $c = 17.1544(17)$ Å; $\beta = 91.406(2)°$, $Z = 4$ for **I**; space group $P2_1/c$ with $a = 12.7150(19)$, $b = 14.000(2)$, $c = 22.171(3)$ Å; $\beta = 96.481(2)°$, $Z = 4$ for **II**. Compound **I** possesses a one-dimensional (1D) zigzag chain structure, each zinc(II) ion is five-coordinated with a distorted triangle bipyramid geometry. Compound **II** is discrete mononuclear species, in which the zinc(II) ion is six-coordinated with a distorted octahedral geometry. The $[Zn(Hpda)_2]^{2-}$ units are connected one-dimensional chain by the intermolecular hydrogen bonds.

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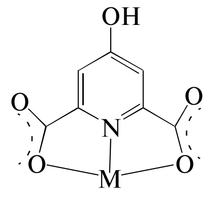
INTRODUCTION

The rational design and construction of novel coordination polymer have attracted much attention in the field of supramolecular chemistry and crystal engineering, due to their intriguing topologies, along with potential applications as a new class of functional solid materials [1–5]. The exploitation of various kinds of organic ligands is of vital importance to increase the structural diversity of coordination polymers, which meanwhile provides new insights into the relationships between the structure and the corresponding function. However, in fact, numerous other factors, such as solvent, concentration, counterion, and temperature may play profound roles in the formation of the thermodynamically favored products [6–10]. Due to pyridinylcarboxamides represent a particularly interesting class of ligands since such simple building unit contains multiple binding sites for the weak interactions. As one of the pyridinylcarboxamides ligands, 2,6-pyridinedicarboxylic acid, have drawn extensive attention. As we know, at present the study of 4-hydroxypyridine-2,6-dicarboxylic acid ($HpdaH_2$) ligand is scarce. In the present paper, we report the syntheses and crystal structures of two new zinc complexes with $HpdaH_2$, $[Zn(Hpda)(Bth\text{-}6)]_{2n}$ (**I**) and $[Zn(Hpda)_2] \cdot 2(H\text{-}Bpe)$ (**II**), whose structures were characterized by elemental analysis, IR spectroscopy and X-ray single-crystal diffraction analysis. The coordination modes of ligand observed in complexes **I** and **II** are illustrated below:



EXPERIMENTAL

Materials and methods. All reagents used in the syntheses were of analytical grade and used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–600 cm^{-1}) were recorded by using KBr pellet on an AvatarTM 360 E.S.P. IR spectrometer. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized Mo radiation ($\lambda = 0.71073$ Å).

Synthesis of I. The mixture of $Zn(OAc)_2 \cdot 2H_2O$ (29.2 mg, 0.1 mmol), $HpdaH_2$ (18.3 mg, 0.1 mmol), Bth-6 (24.5 mg, 0.1 mmol), and in distilled water (8 mL) was sealed in a 25 mL stainless-steel reactor with Teflon liner and heated to 150°C and kept at constant temperature for 72 h. Then the autoclave was cooled at a rate of 2°C h^{-1}, and the colorless block

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	933.52	794.03
Temperature, K	296(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions:		
a, Å	11.9328(12)	12.7150(19)
b, Å	20.975(2)	14.000(2)
a, Å	17.1544(17)	22.171(3)
β, deg	91.406(2)	96.481(2)
Volume, Å^3; Z	4292.3(7); 4	3921.4(10); 4
$\rho_{calculd}$, kg/m^3	1.445	1.345
Crystal size, mm	0.32 × 0.25 × 0.19	0.32 × 0.17 × 0.12
θ Range for data collection, deg	1.53–25.50	2.29–25.50
Reflections collected/unique (R_{int})	22100/7984 (0.0352)	25192/7271 (0.0861)
Goodness-of-fit on F^2	1.097	1.076
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0462$, $wR_2 = 0.1225$	$R_1 = 0.0649$, $wR_2 = 0.1156$
R indices (all data)	$R_1 = 0.0636$, $wR_2 = 0.1344$	$R_1 = 0.1608$, $wR_2 = 0.1307$
Largest diff. peak and hole, e Å^{-3}	0.840 and –0.559	0.456 and –0.344

crystals suitable for X-ray analysis were obtained. Yield was 42% based on Zn.

For $C_{34}H_{38}N_{14}O_{10}Zn_2$			
anal. calcd., %:	C, 43.74;	H, 4.10;	N, 21.00.
Found, %:	C, 43.38;	H, 4.14;	N, 21.12.

Infrared spectrum (KBr; ν, cm^{-1}): 3642, 3614, 1652, 1536, 1455, 1365, 1185, 955, 846, 729.

Synthesis of II. The mixture of $Zn(OAc)_2 \cdot 2H_2O$ (28.8 mg, 0.1 mmol), $HpdaH_2$ (19.1 mg, 0.1 mmol), Bpe (17.6 mg, 0.1 mmol), and in distilled water (8 mL) was sealed in a 25 mL stainless-steel reactor with Teflon liner and heated to 150°C and kept at constant temperature for 60 h. Then the autoclave was cooled at a rate of 2°C h^{-1}, and the colorless block crystals suitable for X-ray analysis were obtained. Yield was 45% based on Zn.

For $C_{38}H_{28}N_6O_{10}Zn$			
anal. calcd., %:	C, 57.48;	H, 3.55;	N, 10.58.
Found, %:	C, 57.56;	H, 3.59;	N, 10.63.

Infrared spectrum (KBr; ν, cm^{-1}): 3647, 3610, 1656, 1532, 1459, 1361, 1182, 952, 841, 722.

X-ray crystallography. Single crystal X-ray diffractions analysis of the two complexes was carried out. Single crystal of the complex **I** or **II** was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using φ–ω scan technique at room temperature. The structures were solved by direct methods with SHELXS-97 [11]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [12]. The final agreement factor values are $R = 0.0462$, $wR = 0.1225$ ($w = 1/[\sigma^2(F_o)^2 + (0.0371P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.097$, $(\Delta/\sigma)_{max} = 0.005$, $(\Delta\rho)_{max} = 0.840$, and $(\Delta\rho)_{min} = -0.559$ e/Å^3 for **I** and $R = 0.0649$, $wR = 0.1156$ ($w = 1/[\sigma^2(F_o)^2 + (0.0304P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.076$, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 0.456$, and $(\Delta\rho)_{min} = -0.344$ e/Å^3 for **II**. Table 1 shows crystallographic crystal data of complexes **I** and **II**. Selected bond lengths and angles are listed in

Table 2. Selected bond distances and angles for **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–N(9)	1.999(2)	Zn(2)–N(2)	1.992(2)
Zn(1)–N(1)	2.000(2)	Zn(2)–N(14)	2.001(2)
Zn(1)–N(3)	2.003(2)	Zn(2)–O(6)	2.1226(19)
Zn(1)–O(3)	2.133(2)	Zn(2)–O(8)	2.214(2)
Zn(1)–O(2)	2.211(2)	N(8)–Zn(2)$^{\#2}$	1.989(2)
		II	
Zn(1)–N(1)	1.991(3)	Zn(1)–O(5)	2.350(3)
Zn(1)–N(2)	1.994(4)	O(1)–C(6)	1.256(5)
Zn(1)–O(1)	2.066(3)	O(2)–C(6)	1.245(5)
Zn(1)–O(10)	2.190(4)	O(3)–C(3)	1.327(5)
Zn(1)–O(6)	2.204(4)	O(3)–H(3)	0.8200
Angle	ω, deg	Angle	ω, deg
		I	
N(9)Zn(1)N(1)	118.75(9)	N(8)$^{\#1}$Zn(2)N(2)	121.84(9)
N(9)Zn(1)N(3)	108.67(10)	N(8)$^{\#1}$Zn(2)N(14)	106.70(9)
N(1)Zn(1)N(3)	132.23(9)	N(2)Zn(2)N(14)	131.00(9)
N(9)Zn(1)O(3)	96.68(9)	N(8)$^{\#1}$Zn(2)O(6)	97.62(9)
N(1)Zn(1)O(3)	77.55(8)	N(2)Zn(2)O(6)	77.81(7)
N(3)Zn(1)O(3)	103.31(9)	N(14)Zn(2)O(6)	103.53(9)
N(9)Zn(1)O(2)	99.13(10)	N(8)$^{\#1}$Zn(2)O(8)	99.59(9)
N(1)Zn(1)O(2)	74.77(8)	N(2)Zn(2)O(8)	75.26(7)
N(3)Zn(1)O(2)	93.14(9)	N(14)Zn(2)O(8)	91.48(9)
O(3)Zn(1)O(2)	152.16(7)	O(6)Zn(2)O(8)	152.82(7)
		II	
N(1)Zn(1)N(2)	157.09(14)	O(10)Zn(1)O(5)	88.91(14)
N(1)Zn(1)O(1)	80.06(13)	O(6)Zn(1)O(5)	94.33(13)
N(2)Zn(1)O(1)	122.82(14)	C(6)O(1)Zn(1)	114.3(3)
N(1)Zn(1)O(10)	104.26(16)	C(3)O(3)H(3)	109.5
N(2)Zn(1)O(10)	76.18(19)	O(1)Zn(1)O(5)	152.89(11)
O(1)Zn(1)O(10)	96.31(16)	C(13)O(6)Zn(1)	114.5(4)
N(1)Zn(1)O(6)	103.25(15)	C(10)O(8)H(8)	109.5
N(2)Zn(1)O(6)	76.50(18)	C(14)O(10)Zn(1)	115.2(5)
O(1)Zn(1)O(6)	93.35(15)	C(5)N(1)Zn(1)	124.4(3)
O(10)Zn(1)O(6)	152.01(13)	C(1)N(1)Zn(1)	115.6(3)
N(1)Zn(1)O(5)	72.87(12)	C(12)N(2)Zn(1)	119.2(4)
N(2)Zn(1)O(5)	84.27(12)	C(8)N(2)Zn(1)	118.5(4)

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

Table 3. Geometric parameters of hydrogen bonds for **II***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	d(D···A)	
O(3)–H(3)···N(6)$^{\#1}$	0.82	1.87	2.653(4)	160
N(4)–H(4*D*)···O(4)$^{\#2}$	0.86	1.91	2.765(5)	175
N(4)–H(4*D*)···O(5)$^{\#2}$	0.86	2.46	3.048(6)	126
N(5)–H(5*D*)···N(3)$^{\#3}$	0.86	1.87	2.724(5)	176

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

Table 2. Hydrogen bond interactions for **II** are given in Table 3.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 978462 (**I**) and 978463 (**II**); deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

X-ray single crystal diffraction analysis reveals that compound **I** exhibits a 1D coordination motif. The asymmetric unit consists of two Zn^{2+} ions, two $Hpda^{2-}$ ligands, and two Bth-6 molecules (Fig. 1). Both Zn centers show similar five-coordination with a distorted triangle bipyramidal geometry, where the equatorial coordination comes from three nitrogen atoms from one $HpdaH_2$ ligand and two distinct Bth-6 ligands, the axial position is occupied by two oxygen atoms from a identical $HpdaH_2$ ligand. The hydroxyl group at the 4-position of $HpdaH_2$ does not take part in metal coordination. The Zn–O distances vary from 2.1226(19) to 2.214(2) Å, and the Zn–N bond lengths are 1.989(2) and 2.003(2) Å, respectively (Table 2), which are within the normal ranges found in other zinc complexes [13–15]. The bond angles involving a metal center are all different and deviate from an ideal triangle bipyramidal coordination geometry. Each Bth-6 ligand joins two Zn^{2+} ions to make a 1D zigzag chain structure with a period of 16.025 Å (Fig. 2).

X-ray single crystal diffraction analysis reveals that compound **II** exhibits discrete mononuclear species. The compound **II** contains one Zn^{2+} ion, two $Hpda^{2-}$ ligands, and two uncoordinated $H\text{-}Bpe^{+}$ molecules. As shown in Fig. 3, the Zn(II) atom is six-coordinated with distorted octahedral coordination geometry by four oxygen atoms (O(1), O(5), O(6), O(10)) and two nitrogen atoms (N(1), N(2)) from two different $HpdaH_2$ ligands. The hydroxyl group at the 4-position of $HpdaH_2$ does not also take part in metal coordination. The Zn(1)–O(1), Zn(1)–O(5), Zn(1)–O(6), and Zn(1)–O(10) bond lengths are 2.066(3), 2.350(3), 2.204(4), and 2.190(4) Å, respectively. The Zn(1)–N(1) and Zn(1)–N(2) bond distances are 1.991(3) and 1.994(4), respectively. In compound **II**, there is the proton transfer phenomenon. A proton from a carboxylic acid is transferred to the nitrogen atom of Bpe molecule. Therefore, Bpe molecule is changed to $H\text{-}Bpe^{+}$ ion. In addition, extensive intermolecular hydrogen bonds formed by the carboxyl group in the $Hpda^{2-}$ ligands and uncoordinated $H\text{-}Bpe^{+}$ ions link the discrete $[Zn(Hpda)_2]^{2-}$ unit to the 1D linear chain (Fig. 4).

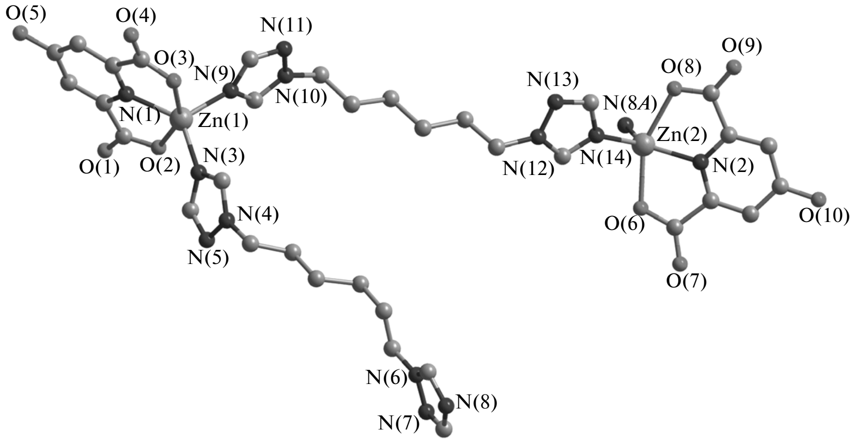

Fig. 1. Coordination environment of Zn(II) atoms (symmetry codes: (*A*) *x*, *y*, 1 + *z*) in complex **I**.

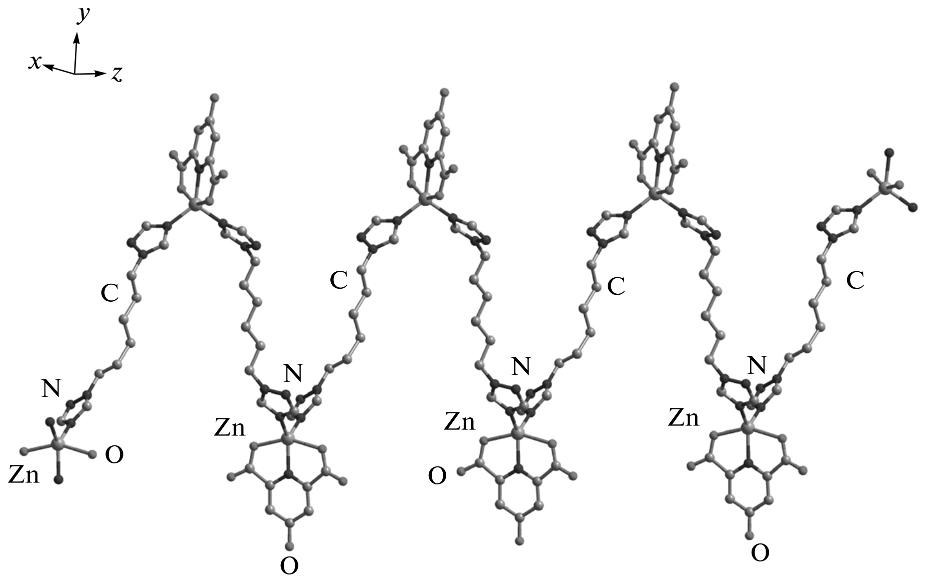

Fig. 2. 1D zigzag chain coordination motif of **I**.

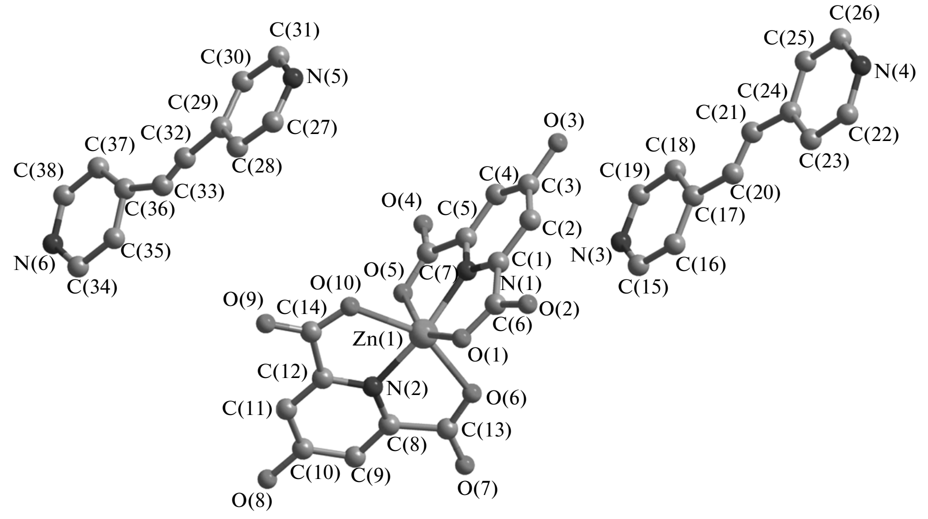

Fig. 3. View of crystal structure of **II**.

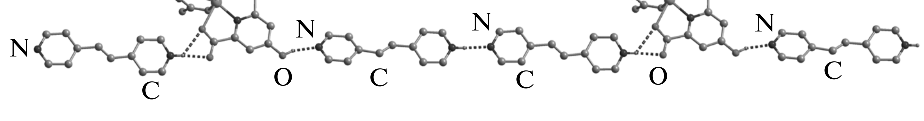

Fig. 4. 1D chain structure constructed via O–H···O interactions in complex **II**.

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