ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 4, pp. 316–320. © Pleiades Publishing, Ltd., 2013.

Hydrothermal Synthesis and Structural Characterization of a New One-Dimensional Ladder-Shaped Metal-Organic Framework $Zn(HTci)(4,4'\text{-}Bipy)_{0.5} \cdot H_2O$ (H_3Tci = Tri(2-Carboxyethyl)isocyanurate, 4,4'-Bipy = 4,4'-Bipyridine)[1]

L. Cui[a, b] **and P. Ch. Zhao**[c, *]

[a] Key Laboratory of Evidence Science (China University of Political Science and Law),
Ministry of Education, Beijing, 100088 P.R. China

[b] Department of Document Examination, China Criminal Police University, Shenyang, 110854 P.R. China

[c] Department of Forensic Chemistry, China Criminal Police University, Shenyang, 110854 P.R. China

*e-mail: zpcccpc@ccpc.edu.cn

Received September 30, 2011

Abstract—A new metal-organic coordination polymer, namely, $Zn(HTci)(4,4'\text{-}Bipy)_{0.5} \cdot H_2O$ (**I**) (H_3Tci = tri(2-carboxyethyl)isocyanurate, 4,4'-Bipy = 4,4'-bipyridine), has been synthesized under hydrothermal conditions by the reaction of zinc nitrate, H_3Tci, and 4,4'-Bipy with the presence of H_2O and characterized by elemental analysis, IR and X-ray single-crystal diffraction. The X-ray diffraction analysis reveals that **I** crystallizes in the triclinic system, $P\bar{1}$ space group. The unit cell parameters for **I**: $a = 5.248(1)$, $b = 12.537(2)$, $c = 14.597(2)$ Å, $\alpha = 91.91(1)°$, $\beta = 91.22(2)°$, $\gamma = 95.75(1)°$, $V = 954.8(3)$ Å^3, $Z = 2$.

DOI: 10.1134/S1070328413040040

INTRODUCTION

The design and synthesis of metal-organic coordination polymers (MOCPs) or metal-organic frameworks (MOFs) have attracted considerable attention in recent decades, not only because of their versatile intriguing architectures and topologies but also owing to their potential applications as functional materials, such as porous materials, catalysis, and magnetic materials [1–9]. However, it is still hard to rationally design the MOCPs or MOFs with desired properties and esthetical structures *via* the mixed organic ligands [10], because the self-assembly process is spontaneously generated from their component organic ligands and metal ions and influenced by several factors, such as the metal/organic ligands nature, solvent, templates, and counter ions [11–14]. It is well known that 1,3,5-tris(4-carboxyphenyl)benzene and 1,3,5-benzenetricarboxylic acid as good candidates for rigid tripodal ligands have been widely employed in the construction of MOCPs or MOFs [15, 16]. However, only a few of them are constructed by the flexible tri(2-carboxyethyl)isocyanurate (H_3Tci) tripodal ligand [17–24]. In this paper, we report the synthesis and crystal structures of $[Zn(HTci)(4,4'\text{-}Bipy)_{0.5} \cdot H_2O]_n$ (**I**) (4,4'-Bipy = 4,4'-bipyridine), which displays a new 1D ladder-shaped chain structure.

EXPERIMENTAL

Materials and methods. All 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.

Solvothermal synthesis. A reaction mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.119 g, 0.4 mmol), H_3Tci (0.069 g, 0.2 mmol), 4,4'-Bipy (0.016 g, 0.1 mmol) and distilled water (8 mL) was added to a 23 mL Teflon-lined stainless steel autoclave, which was stirred at room temperature until the mixture became homogeneous. The autoclave was sealed and heated under autogenous pressure at 403 K for four days, followed by slow cooling (5 K h^{-1}) to room temperature. The colorless block crystals of **I** were isolated by filtration, washed with distilled water and dried in air (yield is ~40%). Complex **I** is insoluble in water and common organic solvents, such as DMF, DMSO, CH_3CN, benzene, toluene, methanol, ethanol, acetone, and propanol.

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[1] The article is published in the original.

IR (KBr; ν, cm^{-1}): 3448 s, 2426 w, 1690 s, 1610 s, 1384 v.s, 840 s, 747 s, 530 w.

For $C_{17}H_{18}N_4O_{10}Zn$			
anal. calcd., %:	C, 40.53;	H, 3.60;	N, 11.12.
Found, %:	C, 40.57;	H, 3.45;	N, 11.10.

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 [25]. 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. Hydrogen bonding geometric data is listed in Table 3. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 831888; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The asymmetric unit including one Zn^{2+} ion, one $HTci^{2-}$ unit, half 4,4'-Bipy ligand, and one metal-bound water molecule. As illustrated in Fig. 1, the Zn^{2+} ion is four-coordinated by one nitrogen atom (N(4)) from one 4,4'-Bipy ligand and three oxygen atoms (O(1), O(6*A*), O(1*w*)) from two individual $HTci^{2-}$ ligands and one water molecule, respectively. The coordination environment around the Zn(II) center can be described as a slightly distorted tetrahedral geometry with bond lengths from 1.9639(19) (Zn(1)–O(6*A*)) to 2.040(2) Å (Zn(1)–N(4)) and the bond angles ranging from 95.80(8)° (O(6*A*)Zn(1)O(1)) to 121.91(9)° (O(6A)Zn(1)N(4)) (Table 2). The adjacent Zn(II) centers are bridged by rigid linear 4,4'-Bipy ligands and by flexible two arms of HTci ligands with the Zn···Zn separations of 11.1871(17) and 13.0972(23) Å, respectively, forming a one-dimensional (1D) ladder-shaped chain (Fig. 2). The π–π stacking interaction is observed between two pyridine rings of the 4,4'-Bipy ligands with a perpendicular separation of 3.0903(11) Å, a centroid-to-centroid distance of 5.277(2) Å and a slippage of 4.277°. These values are typical of aromatic π–π stacking interactions [26]. Adjacent chains are further connected *via* strong O–H···O hydrogen bonds and weak C–H···O hydrogen bonds to form a three-dimensional (3D) supramolecular framework (Table 3, Fig. 3). These interactions enhance the stability of complex.

IR spectrum was recorded with KBr pellets in the range of 4000–400 cm^{-1}. The ν(O–H) vibration of the

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

Parameter	Value
Formula weight	503.72
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a, Å	5.2480(11)
b, Å	12.537(2)
c, Å	14.597(2)
α, deg	91.911(13)
β, deg	91.219(15)
γ, deg	95.749(14)
V, $Å^3$	954.8(3)
Z	2
ρ_{calcd}, mg cm^{-3}	1.752
Absorption coefficient, mm^{-1}	1.355
F(000)	516
Crystal size, nm	0.37 × 0.32 × 0.26
θ Range, deg	1.63–26.01
Limited indices *h*, *k*, *l*	$-1 \le h \le 6$, $-15 \le k \le 15$, $-17 \le l \le 17$
Reflections collected	5042
Independent reflections (R_{int})	3765 (0.0301)
Reflections with $I > 2\sigma(I)$	3326
T, K	293(2)
GOOF	1.137
Parameters	289
Final *R* indices ($I > 2\sigma(I)$)*	$R_1 = 0.0324$, $wR_2 = 0.0898$
R indices (all data)	$R_1 = 0.0427$, $wR_2 = 0.1030$
Largest diff. peak and hole, *e* $Å^{-3}$	0.7212 and 0.6354

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

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

Bond	*d*, Å	Bond	*d*, Å
Zn(1)–O(6)$^{\#1}$	1.9639(19)	Zn(1)–O(1)	2.0035(19)
Zn(1)–O(1*w*)	1.967(2)	Zn(1)–N(4)	2.040(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(6)$^{\#1}$Zn(1)O(1*w*)	111.44(9)	O(6)$^{\#1}$Zn(1)N(4)	121.91(9)
O(6)$^{\#1}$Zn(1)O(1)	95.80(8)	O(1*w*)Zn(1)N(4)	107.78(9)
O(1*w*)Zn(1)O(1)	107.79(9)	O(1)Zn(1)N(4)	110.99(9)

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

Table 3. 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		
O(1*w*)–H(1*w*)···O(1)	0.85	1.84	2.680(3)	172	$1 + x, 1 + y, z$
O(1*w*)–H(1*wB*)···O(6)	0.85	2.03	2.774(3)	146	$-x, 1 - y, 2 - z$
C(4)–H(4*A*)···O(2)	0.97	2.46	2.818(3)	102	x, y, z
C(4)–H(4*A*)···O(8)	0.97	2.37	2.740(4)	102	x, y, z
C(10)–H(10*A*)···O(9)	0.97	2.37	2.751(3)	103	x, y, z
C(10)–H(10*B*)···O(7)	0.97	2.42	3.269(3)	146	$-1 - x, 1 - y, 2 - z$
C(13)–H(13*A*)···O(4)	0.93	2.36	3.102(3)	136	$-x, 1 - y, 1 - z$
C(16)–H(16*A*)···O(9)	0.93	2.58	3.239(4)	128	$2 + x, 1 + y, z$
C(17)–H(17*A*)···O(5)	0.93	2.53	3.143(4)	124	$1 + x, 1 + y, z$

water molecules in **I** is observed at about 3448 cm^{-1}. The bands at 1610 and 1384 cm^{-1} correspond to the asymmetric and symmetric stretching for carboxyl groups, respectively. The values of $\Delta(\nu_{as} - \nu_s) = 226$ cm^{-1} (>200 cm^{-1}) demonstrates the monodentate coordination mode of all the carboxylic groups to the Zn^{2+} ion [27, 28]. The existence of strong characteristic peaks at 1690 cm^{-1} indicates that carboxylic group is partly protonated, which is consistent with the results of the X-ray analysis.

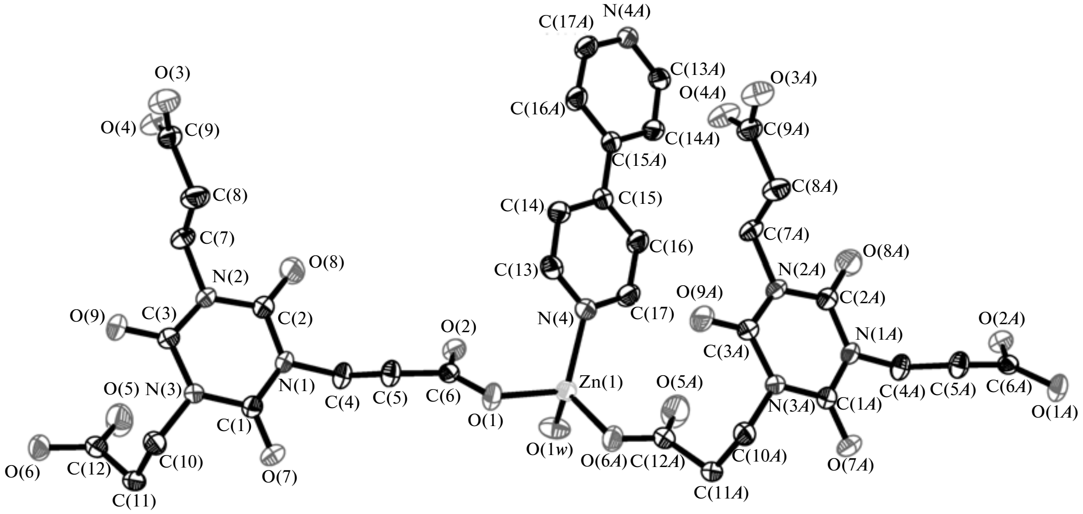

Fig. 1. Coordination environment of the Zn^{2+} ion in **I**.

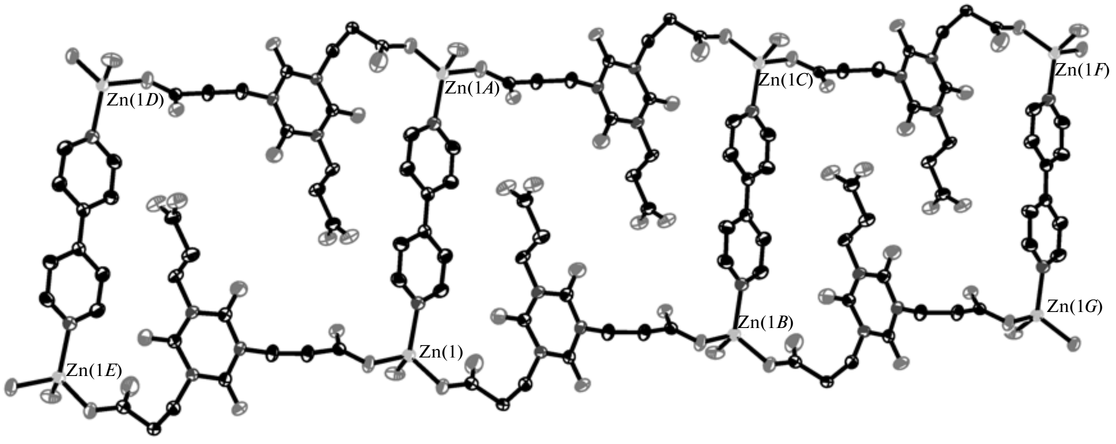

Fig. 2. Fragment of 1D ladder-shaped chain structure in **I**.

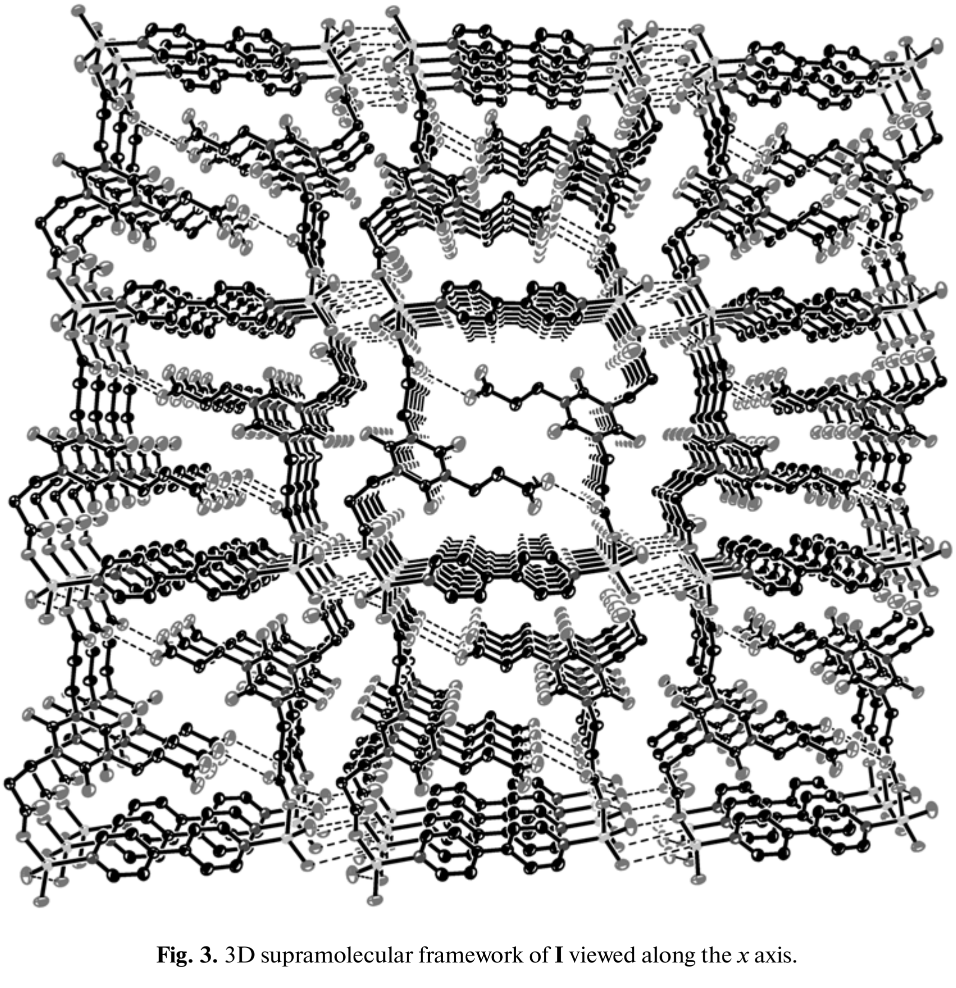

Fig. 3. 3D supramolecular framework of **I** viewed along the *x* axis.

ACKNOWLEDGMENTS

This work was supported by the Opening Project of Key Laboratory of Evidence Science (China University of Political Science and Law), Ministry of Education (2011KFKT03), and PhD Initial Funding Project of Liaoning Province (no. 2010010174-401).

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