ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 1, pp. 59–63. © Pleiades Publishing, Ltd., 2018.

Synthesis, Crystal Structure, and Characterization of One 1D Complex in $Ni^{2+}/H_4L/p$-Bix System (H_4L = Methylenediisophthalic Acid, p-Bix = 1,4-Bis(Imidazol-1-Ylmethyl)-Benzene)[1]

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Received April 17, 2017

Abstract—Under hydrothermal condition, one 1D Ni(II) complex has been prepared. The result of X-ray diffraction analysis (CIF file CCDC no. 972293) shows that in this complex both Ni(II) atoms adopt six-coordinated mode. First, L is coordinated to four Ni(II) atoms to form 1D $[(Ni_2(L))]_\infty$ (H_4L = methylenediisophthalic acid) chain. Then, p-Bix = 1,4-bis(imidazol-1-ylmethyl)-benzene (p-Bix) ligands are decorated alternatively on both sides of 1D $[(Ni_2(L))]_\infty$ chain to be 1D $[(Ni_2(L))(p\text{-Bix})]_\infty$ chain. Finally, relying on weak interactions, such as hydrogen bonds and π···π stacking interactions, the complex exhibits 3D supramolecular framework. Moreover, at room temperature, the IR spectrum, PXRD and TG analyses were employed to characterize the complex.

Keywords: coordination complex, 1D chain, crystal structure

DOI: 10.1134/S1070328418010037

INTRODUCTION

Coordination complexes constructed with a variety of metal ions and polytopic bridging ligands [1] are of great interest in recent years, and have been used in a wide range of applications, including selective gas sorption, heterogeneous catalysis, separation, sensor, drug delivery [2–5]. Rational design and synthesis of coordination polymers have stimulated a wide range of research interests over the past few decades owing to their rich structural aesthetics and functionalities.

Multicarboxylates have been commonly used in metal organic frameworks, giving structures of various dimensionalities with different coordination modes and pore size. Metal-carboxylate units can act as secondary building units in the construction of various interesting topologies [6]. Lately, there has been a conscientious effort to incorporate a secondary auxiliary ligand into the final metal carboxylate product. A great deal of mixed-ligand coordination polymers involved in flexible N-donor bridging ligands, such as bis(pyridine), bis(imidazole), bis(tetrazole) ligands, have been reported [7–9]. These ligands could bend or rotate freely and feature various coordination conformations during the assembly with metal centers, which usually result in structural diversities. Among many strategies for constructing coordination polymers, the self-assembly of neutral N-heterocyclic ligands and polycarboxylates with metal ions under hydro(solvo)thermal conditions has become one of the most effective approaches.

As an extension of our previous work, we introduce p-Bix = 1,4-bis(imidazol-1-ylmethyl)-benzene (p-Bix) ligand into $Ni^{2+}-H_4L$ (H_4L = methylenediisophthalic acid) system and obtain one interesting 1D coordination polymer $[(Ni_2(L))(p\text{-Bix})(H_2O)_3]_2 \cdot 5H_2O$ (**I**), which is different from the reported 2D layer in Zn–H_4L–p-Bix [10] and Co–H_4L–p-Bix system [11]. The crystal structure **I**, IR spectrum and PXRD patterns were characterized at room temperature.

EXPERIMENTAL

General procedures and instrument. H_4L, p-Bix were prepared according to the literatures [12, 13]. All other starting materials were of reagent quality and obtained from commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a RigakuD/max-RA rotating anode X-ray diffractometer with graphite-monochromatized CuK_α (λ = 1.542 Å) radiation at room temperature. Thermal analyses were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinements for complex **I**

Parameter	Value
Fw	1549.92
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	9.8762(16)
b, Å	12.884(2)
c, Å	13.107(2)
α, deg	87.596(4)
β, deg	81.661(2)
γ, deg	74.996(3)
V, Å^3	1593.9(4)
Z	1
ρ_{calcd}, g cm^{-3}	1.615
T, K	291(2)
μ, mm^{-1}	1.255
F(000)	798.0
Reflections collected/unique	8667/6124
R_{int}	0.0598
GOOF on F^2	1.116
R_1/wR_2 ($I > 2\sigma(I)$)	0.0824/0.1277
Largest diff. peak and hole, *e* Å^{-3}	0.606 and –0.733

800°C with a heating rate of 20°C/min in a nitrogen environment.

Synthesis of complex I was carried out by hydrothermally in a 25 mL Teflon-lined autoclave by heating a mixture of 0.1 mmol H_4L, 0.1 mmol *p*-Bix, 0.2 mmol $Ni(NO_3)_2 \cdot 6H_2O$, methanol (2 mL), H_2O (8 mL) and one drop of triethylamine (Et_3N) at 120°C for 3 days. Green single crystals were collected in 78% yield on the basis of nickel.

For $C_{62}H_{58}N_8O_{25}Ni_4$			
anal. calcd., %	C, 48.04	H, 3.77	N, 7.23
Found, %	C, 47.95	H, 3.68	N, 7.28

IR (KBr; ν, cm^{-1}): 3422 s, 3126 m, 2929 w, 2853 w, 1610 s, 1548 s, 1521 s, 1437 s, 1373 s, 1239 m, 1109 m, 1034 w, 985 w, 952 w, 898 w, 817 w, 778 m, 725 m, 651 m, 574 w, 448 w.

X-ray crystallography. Single crystal suitable for X-ray analysis was used on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at room temperature using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structure was solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [14]. Anisotropicthermal parameters were assigned to all nonhydrogen atoms. Crystal data and details of the structural determinations for complex **I** are listed in Table 1, selected bond lengths and angles are listed in Table 2 and hydrogen bonds are listed in Table 3.

RESULTS AND DISCUSSION

It has been reported that the Zn–H_4L–*p*-Bix system is 2D layer structure, when the metal center is nickel atom, the resulting complex shows different structure. That is, the Ni–H_4L–*p*-Bix leads to the formation of a 1D linear structure in $[(Ni_2(L))(p\text{-}Bix)(H_2O)_3]_2 \cdot 5H_2O$.

As revealed by single-crystal X-ray crystallography, the structure of **I** is constructed from the following structural elements: one L^{4-}, one *p*-Bix, two metal centers, three coordinated and 2.5 lattice water molecules. Two Ni^{2+} cations are all six-coordinated with

Table 2. Related bond lengths and angles in complex **I***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Ni(1)–O(10)	2.068(3)	N(1)–Ni(1)	2.042(4)	Ni(1)–O(1)	2.306(3)
Ni(1)–O(2)	2.051(3)	Ni(1)–O(5)$^{\#2}$	1.973(3)	Ni(1)–O(9)	2.083(3)
Ni(2)–O(3)	2.033(3)	N(4)–Ni(2)	2.015(4)	Ni(2)–O(4)	2.206(3)
Ni(2)–O(8)$^{\#1}$	2.065(3)	Ni(2)–O(11)	2.056(3)	Ni(2)–O(7)$^{\#1}$	2.139(3)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(10)Ni(1)O(9)	171.86(12)	O(5)$^{\#2}$Ni(1)O(2)	162.69(12)	O(11)Ni(2)O(7)$^{\#1}$	157.02(12)
N(1)Ni(1)O(1)	153.59(13)	N(4)Ni(2)O(4)	158.35(13)	O(3)Ni(2)O(8)$^{\#1}$	160.36(12)

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

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

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(9)–H(9*A*)···O(12)$^{\#1}$	0.85	2.17	2.943	152
O(9)–H(9*B*)···O(7)$^{\#2}$	0.85	2.03	2.880	173
O(10)–H(10*C*)···O(8)$^{\#3}$	0.85	2.05	2.855	159
O(10)–H(10*B*)···O(6)$^{\#4}$	0.85	1.81	2.578	148
O(12)–H(12*A*)···O(3)	0.85	1.98	2.827	178

* Symmetry codes: $^{\#1}$ $-x, -y+1, -z+1$; $^{\#2}$ $x, y-1, z$; $^{\#3}$ $x+1, y-1, z$; $^{\#4}$ $-x, -y+1, -z$.

different coordination environment (Fig. 1). Ni(1) is coordinated by one mono-carboxylate and one chelating carboxylate from L^{4-}, one *p*-Bix ligand and two coordinated water molecules. Ni(2) is coordinated by two mono carboxylates and one chelating carboxylates from L^{4-}, one *p*-Bix ligand and one coordinated water molecule. The Ni–O bond lengths range between 1.973(3) and 2.306(3) Å, while the Ni–N bond lengths are 2.015(4) and 2.042(4) Å (Table 2). As shown in Fig. 1, the geometry of Ni(2) is greatly distorted from the octahedron of Ni(1). All the bond lengths and angles are within the normal range [15, 16].

Seen from Fig. 2a, left, along *y* direction using mono and chelating coordination carboxylates, each L^{4-} connects four nickel centers to generate 1D $[Ni_2(L)]_\infty$ chain, in which the separation of Ni(1)···Ni(1)$^{\#1}$, Ni(1)···Ni(2), Ni(2)···Ni(2)$^{\#2}$, Ni(1)$^{\#1}$···Ni(2)$^{\#2}$ are 8.00, 8.86, 9.88, 10.08 Å, respectively. The dihedral angle of L^{4-} two aryl rings is 73.04°. The methylene of L^{4-} is bending up and down the 1D chain (Fig. 2a right), so there exists a grid void along [0 1 1] plane with the dimensional of 6.34 × 8.00 Å. *P*-Bix ligands are decorated alternatively on both sides of the 1D chain and terminate the 1D chain extension in *z* axis. As for the *trans p*-Bix, the terminal imidazole groups have their planes tilted by 71.34°, 67.66°, respectively, with respect to the average plane of the phenyl ring, and two pairs of imidazole groups twisted by 58.39°.

Along *z* direction, adjacent chains are packed through two kinds of π···π stacking effects, giving rise to 2D network (Fig. 2c): (I) between the *p*-Bix ligands and L^{4-} with centroid-to-centroid distances of ~3.70 Å, and the two aryl rings are twisted by 10.68°; (II) between of parallel L^{4-} aryl rings of adjacent chains with centroid-to-centroid distances of ~3.52 Å. In addition, hydrogen bonds lie between free water molecule and carboxylates of L^{4-}. As shown in Fig. 2b, hydrogen bonds between carboxylates and coordinated water molecules extended 2D framework of adjacent layers in *z* and *x* direction (Table 3) to be 3D supramolecular architecture. Comparing the 2D layer in $Zn^{2+}(Co^{2+})$–H_4L–*p*-Bix with the 1D chain in

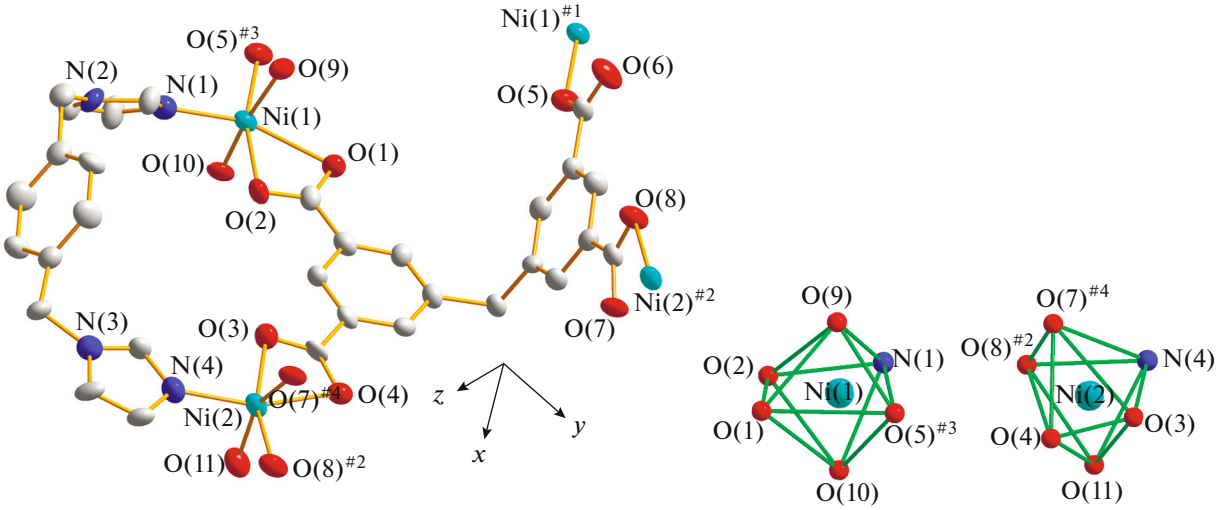

Fig. 1. Coordination environments of the Ni^{2+} ions in complex **I** (symmetry codes: $^{\#1}$ $-x, 1-y, -z$; $^{\#2}$ $-x, 2-y, 1-z$; $^{\#3}$ $-x, 1-y, -z$; $^{\#4}$ $-x, 2-y, 1-z$).

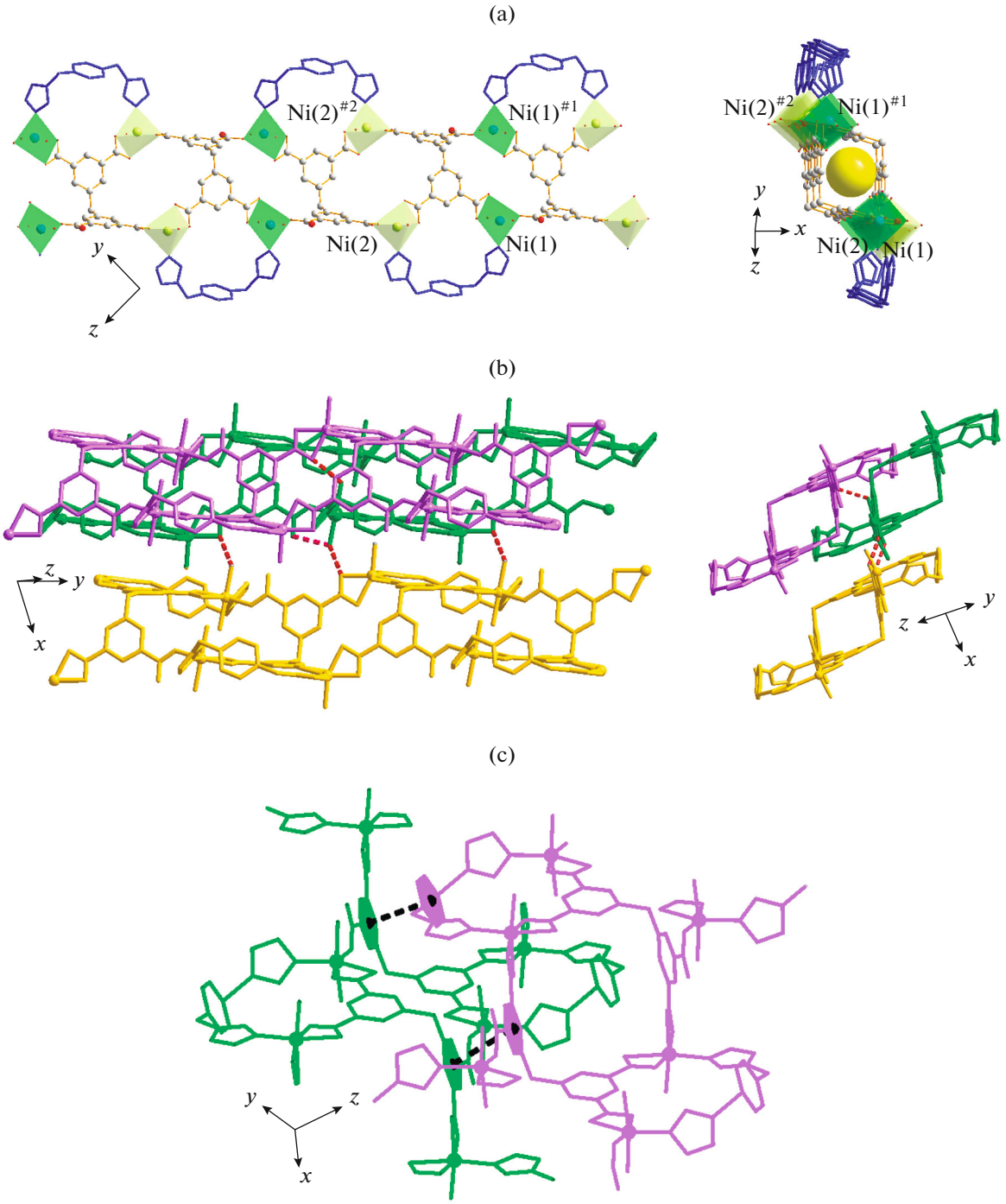

Fig. 2. View of 1D chain $[(Ni_2(L))(p\text{-Bix})(H_2O)_3]_\infty$ in complex **I** (a) (symmetry codes: #1 $-x$, $1-y$, $-z$; #2 $-x$, $2-y$, $1-z$); representation of hydrogen bonds between adjacent $[(Ni_2(L))(p\text{-Bix})(H_2O)_3]_\infty$ chains (b); representation of π···π stacking interactions of adjacent chains in z direction (c).

Ni^{2+}–H_4L–*p*-Bix, their structural difference is much related to the nature of the metal center.

The IR spectra of complex **I** showing strong absorption bands between 1350 and 1630 cm^{-1} can be assigned to coordinated carboxylate groups [17]. The broad but strong absorption at 3350–3500 cm^{-1} corresponds to the presence of water molecules in complex **I**. The absence of bands around 1700 cm^{-1} in complex **I** indicates the complete deprotonation of H_4L. All this agrees well with the result of X-ray single-crystal analysis.

The observed PXRD patterns are consistent with simulated conditions using single crystal X-ray diffraction, and confirmed that the structure reported is

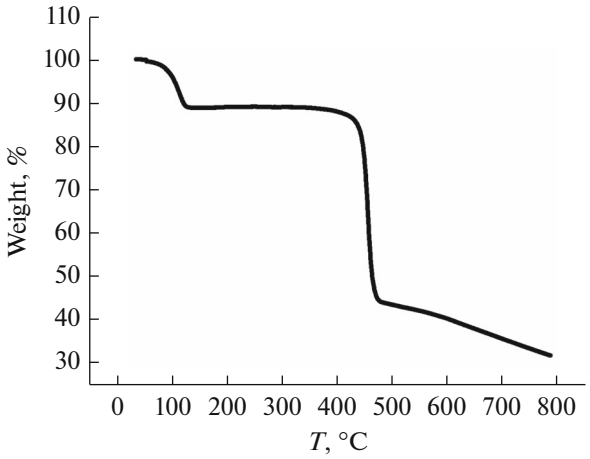

Fig. 3. TGA curve of complex **I**.

representative of the bulk materials. The difference in the intensity may be related to the different orientation of the powder samples.

To characterize the complex more fully in terms of thermal stability, the thermal behaviors were studied by TGA, and the result is shown in Fig. 3. A total weight loss of 12.06% was observed for the title complex below 150°C, which was attributed to the release of free and coordinated water molecules (calcd. 12.77%). It does not lose weight until ~350°C. After that, the residue began to decompose.

Thus, under hydrothermal conditions, one interesting 1D chain in the Ni^{2+}–H_4L–*p*-Bix system has been obtained, which is a mononuclear coordination polymer. L^{4-} and Ni^{2+} are joined together to be 1D infinite chain $[Ni_2(L)]_\infty$, and the methylene orientation of L^{4-} subsequently are bent up and down. Then, *p*-Bix ligands decorated on both sides of $[Ni_2(L)]_\infty$ chain to be 1D $[(Ni_2(L))(p\text{-Bix})]_\infty$ chain. Hydrogen bonds and π···π stacking interactions are attributed to the formations of 3D supramolecular framework.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (grant no. 21501047).

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