ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 5, pp. 367–372. © Pleiades Publishing, Ltd., 2009.

Synthesis, Crystal Structure, and Catalytic Properties of a One-Dimensional Nickel(II) Polymer[1]

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Received July 10, 2008

Abstract—The title complex $[Ni_2(C_{10}H_9N_3)_2(C_{14}H_8O_5)_2]_n$, which has an inversion center, midway between two Ni(II) atoms forms a one-dimensional polymer bridged by 4,4'-oxydibenzoate ligands with a Ni···Ni separation of 14.4705(11) Å. The Ni(II) atom is six-coordinated by two N atoms of a bis(2-pyridyl)amine ligand and four O atoms from two 4,4'-oxydibenzoate ligands, to form a distorted octahedron coordination geometry and then are linked via N–H···O and C–H···O hydrogen bonding into a polymeric ribbon structure. The activity and selectivity profiles of the polymer indicate that the optimization temperature and time span are 175°C and 30–40 min for the dehydration of cyclohexanol, respectively.

DOI: 10.1134/S1070328409050091

INTRODUCTION

The design and synthesis of metal-organic coordination polymers have captured the extensive interest of researchers in supramolecular chemistry owing to their novel topologies and potential applications, such as magnetism, catalysis, molecular recognition, electrical conductivity, adsorption, separation, and biology [1–5]. As commonly accepted, the generation of supramolecular architectures relies on the combination of several factors, such as the coordination geometry of metals, organic building blocks, and reaction conditions. Especially, the judicious choice of appropriate ligand is one of the crucial effects on the structures and functionality for the complexes formed [6, 7]. Among the synthetic strategies to achieve these polymeric compounds, the bridging ligands play an important role in forming the structure of coordination polymer. As is well known, bridging ligands containing bi- or multidentate oxygen, nitrogen, or sulfur donors as building blocks have ever been used in the construction [8–10]. In order to successfully prepare transitional metals coordination polymers, a good strategy is the assembly reaction between a transitional metal ion and two types of ligands with one acting as a bridging ligand and the other as a terminal ligand. For example, one ligand containing carboxylate groups is popularly used in synthetic systems for the construction of polymeric structures because of their various coordination modes to metal cations, such as monodentate, chelating bidentate, bridging bidentate, and bridging tridentate [11–13]. Another chelating ligand containing pyridyl, which usually exhibits donor as well as acceptor properties, is introduced to occupy the uncoordinated sites of metal center and provide the potential π–π stacking interactions, which favor the generation of the crystallized product [14–16].

Recently, more and more interest has focused on long flexible ligands, such as the 4,4'-oxybisbenzoic acid ligand. The two benzene moieties are linked together by a μ-O bridge, which displays the advantages of no branched chain, small steric hindrance, and better bridging action. Due to these advantages, in the self-assembly process it is the typical example of flexible a ligand and may offer more possibilities in geometry configuration and coordination modes toward the metal ions [17, 18]. In addition, bis(2-pyridyl)amine as a versatile ligand due to its conformational flexibility can act in N,N'-bidentate or bridging coordination modes toward many metals, resulting in complexes with different stereochemistry, or act in an N,N',N''-coordination mode as a tridentate ligand [19–21]. However, the one-dimensional dinuclear coordination polymers including synchronously two above types of ligands remains unexplored. Consequently, we have selected the bridging ligand 4,4'-oxybisbenzoic acid, chelating bidentate ligand bis(2-pyridyl)amine and Ni^{2+} ion with appropriate geometry as the research system to explore potential metal-organic frameworks. Herein, we report the synthesis, structure, and catalytic proper-

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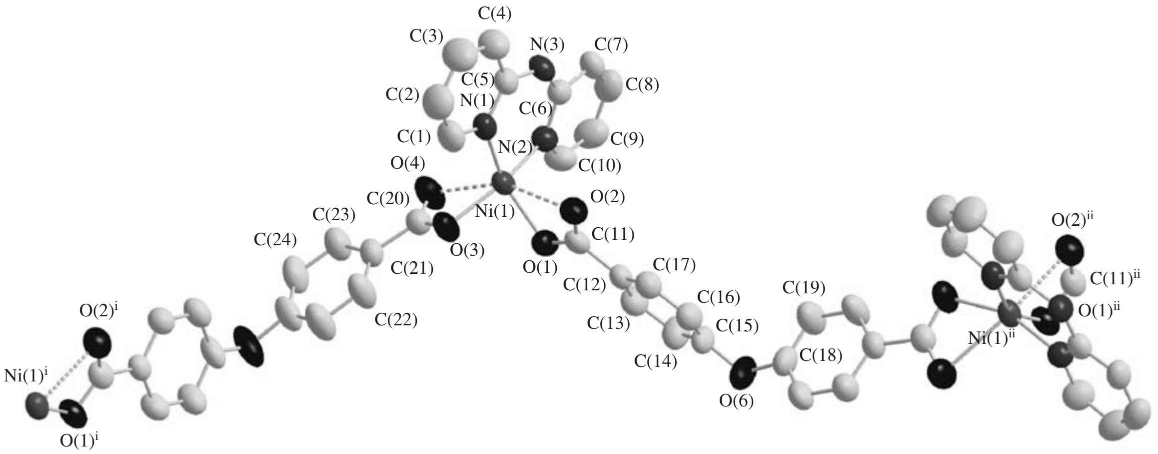

Fig. 1. Molecular structure of the title complex **I** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level (symmetry code: ^{i} $x + 1, -y + 1/2, z + 1/2$; ^{ii} $x - 1, -y + 1/2, z - 1/2$). All H atoms are omitted for clarity.

ties of a one-dimensional polymeric nickel(II) compound $[Ni_2(C_{10}H_9N_3)_2(C_{14}H_8O_5)_2]_n$ (**I**).

EXPERIMENTAL

Apparatus and reagents. All the reagents and solvents from commercial sources were of AR grade purity. Element analysis of carbon, hydrogen, and nitrogen was performed with a Flash-EA1112 elemental analyzer. The catalytic activity tests were performed at atmospheric pressure in an automatic micromeritics flow reactor. The dehydration of cyclohexanol was investigated in the range 140–200°C. The ambient temperatures for columns and FID were 50 and 100°C, respectively. The conversion was assigned as a measure of catalytic activity.

A green single crystal with dimensions of $0.30 \times 0.08 \times 0.04$ mm was selected for diffraction analysis. Data collection was performed on a Bruker APEX-II CCD area-detector diffractometer equipped with a graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 273(2) K. A total of 14137 reflections were collected by using an ω–2θ scan mode, of which 4323 were unique with $R_{int} = 0.0609$ and used in the succeeding structure calculations. Data intensity was corrected by the Lorentz polarization factors and empirical absorption. The non-hydrogen atoms were solved by direct methods and subsequent difference Fourier synthesis. The hydrogen atoms were calculated in ideal positions and refined with a riding model. The final cycle of full-matrix least-squares refinement was based on 2067 observed reflections ($I > 2\sigma(I)$) and 303 variable parameters and converged with weighed agreement factors. The final refinement including hydrogen atoms converged to 0.0371 and $wR = 0.0482$ ($w = 1/[\sigma^2(F_o^2) + (0.0091P)^2 + 0.0800P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.003$, $(\Delta/\sigma)_{max} = 0.001$, $(\Delta\rho)_{max} = 0.294$ and $(\Delta\rho)_{min} = -0.493$ e Å^{-3}. All calculations were performed using the SHELXTL-97 program package [22].

Synthesis of the complex. Crystals of the title complex were synthesized using the solvothermal method in a 23-ml teflon-lined parr bomb, which was then sealed. Nickel dinitrate hexahydrate (145 mg, 0.5 mmol), bis(2-pyridyl)amine (171 mg, 1 mmol), 4,4'-oxybisbenzoic acid (258 mg, 1 mmol), and tetrahydrofuran (8 ml) were placed into the bomb and sealed. The bomb was then heated under autogenous pressure up to 433 K over the course of 7 days and allowed to cool at room temperature for 24 h. Upon opening the bomb, a clear colorless solution was decanted from small green crystals. These crystals were washed with ethanol and allowed to air-dry at room temperature. The yield, as calculated with respect to the nickel dinitrate, was 37.4%.

For $C_{48}H_{34}N_6O_{10}Ni_2$

anal. calcd, %:	C, 59.29;	H, 3.51;	N, 8.65.
Found, %:	C, 59.33;	H, 3.52;	N, 8.68.

RESULTS AND DISCUSSION

The X-ray crystal structure analysis reveals that title complex **I** belongs to monoclinic crystal system, space group $P2_1/c$ with $a = 12.3291(11)$, $b = 15.4906(18)$, $c = 11.2258(12)$ Å, $\beta = 95.997(3)°$, $V = 2132.2(4)$ Å^3, $M_r = 972.24$, $Z = 2$, $\rho_c = 1.514$ g/cm^3, $\mu = 0.953$ mm^{-1}, $F(000) = 1000$. The molecular structure, one-dimensional chain and packing diagram of **I** are shown in Figs. 1–3, respectively. As shown in Fig. 1, molecule of **I** features a dinuclear structure and the Ni(II) atoms are bridged by 4,4'-oxydibenzoate ligands with an inversion center between the two Ni^{2+} ions. Ni(1) is coordinated by one bis(2-pyridyl)amine ligand via N(1) and N(2) atoms, two bridging 4,4'-oxydibenzoate ligands via O(1), O(2), O(3), and O(4), respectively, with a distorted octahedron coordination geometry.

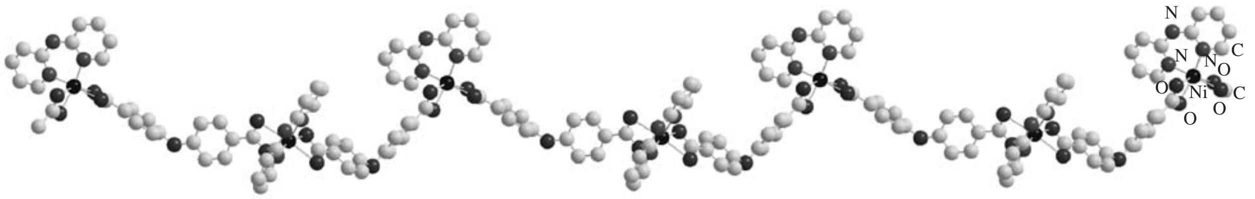

Fig. 2. One-dimensional infinite chain in **I**.

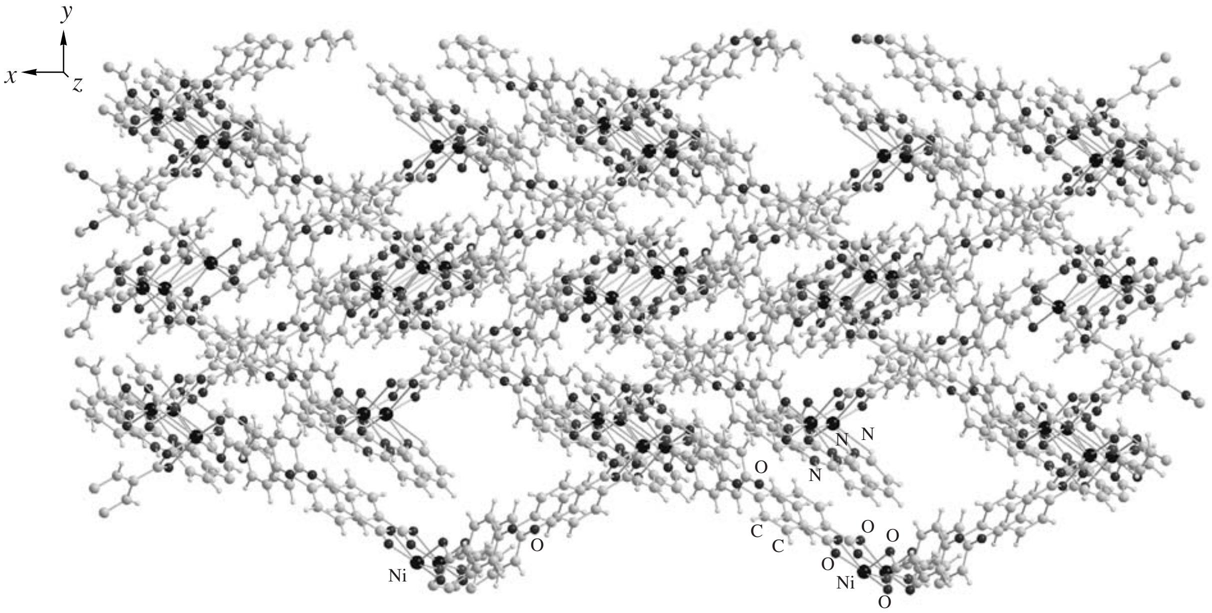

Fig. 3. Packing diagram of **I** linked by hydrogen bonding.

Bond angles O(1)Ni(1)O(2), O(2)Ni(1)N(1), N(1)Ni(1)O(4), and O(4)Ni(1)O(1) are 58.27(6)°, 94.04(7)°, 103.87(7)°, and 102.40(7)° (Table 1), respectively. The sum of angles is 358.58° (close to 360°), suggesting that the basal plane is defined by one nitrogen atom from the chelating bis(2-pyridyl)amine ligand, three carboxylate oxygen atoms from the bridging 4,4'-oxydibenzoate ligands (N(1), O(1), O(2), and O(4)) with the mean deviation of 0.110 Å from the least-squares plane, and the Ni(1) atom deviates by 0.206 Å

Table 1. Selected bond lengths (Å) and bond angles (deg) in **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Ni(1)–O(1)	2.0099(16)	Ni(1)–O(2)	2.4516(18)	Ni(1)–O(3)	1.9873(17)
Ni(1)–O(4)	2.4163(18)	Ni(1)–N(1)	1.987(2)	Ni(1)–N(2)	1.968(2)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Ni(1)O(2)	58.27(6)	O(1)Ni(1)O(3)	91.30(7)	O(1)Ni(1)O(4)	102.40(7)
O(2)Ni(1)O(3)	104.91(7)	O(2)Ni(1)O(4)	155.85(7)	O(3)Ni(1)O(4)	58.03(7)
O(1)Ni(1)N(1)	152.27(7)	O(1)Ni(1)N(2)	91.07(8)	O(2)Ni(1)N(1)	94.04(7)
O(2)Ni(1)N(2)	94.59(7)	O(3)Ni(1)N(1)	95.10(9)	O(3)Ni(1)N(2)	158.37(8)
O(4)Ni(1)N(1)	103.87(7)	O(4)Ni(1)N(2)	100.50(8)	N(1)Ni(1)N(2)	92.74(9)

Table 2. The geometric parameters of hydrogen bonds in **I***

Bond D–H···A	Distances, Å			Angle (DHA), deg
	D–H	H···A	D···A	
C(10)–H(10)···O(1)	0.93	2.50	2.927(4)	109
N(3)–H(3A)···O(2)^{iii}	0.94(2)	1.84(2)	2.779(3)	173(2)

Note: * Symmetry codes: ^{iii} $-x + 1, y + 1, -z + 1$.

out of the plane. Bond angles between N(2) and equator plane atoms (N(1), O(1), O(2), and O(4)) are as follows: O(1)Ni(1)N(2) 91.07(8)°, O(2)Ni(1)N(2) 94.59(7)°, O(4)Ni(1)N(2) 100.50(8)°, and N(1)Ni(1)N(2) 92.74(9)°. All these angles approach 90°, indicating that N(2) is almost located on the centrosymmetric axis of equator plane. Besides, the bond angle O(3)Ni(1)N(2) (158.37(8)°) is biggest and approaches to 180°, illustrating that N(2) and O(3) atoms hold the vertex location.

The Ni–N distances are 1.987(2) and 1.968(2) Å, respectively, which should be attributed to the coordination between the bis(2-pyridyl)amine ligand and the Ni^{2+} ion in the normal chelating manner. The Ni–O distances are from 1.9873(17) to 2.4516(18) Å, and the distances of Ni(1)–O(2) and Ni(1)–O(4) (average 2.434 ± 0.018 Å) are much longer than of Ni(1)–O(1) and Ni(1)–O(3) (average 1.999 ± 0.012 Å), which could be attributed to the semicoordinate between Ni(1) and O(2) or O(4) [23]. It should be noted that the bond distances of O(1)–C(11) (1.271(3) Å) and O(3)–C(20) (1.258(3) Å) are longer than those of O(2)–C(11) (1.257(3) Å) and O(4)–C(20) (1.235(3) Å), in accord with a greater double-bond character of the latter bonds. Furthermore, the pyridyl rings of the bis(2-pyridyl)amine ligands and phenyl rings of the 4,4'-oxydibenzoate ligands are twisted to meet the requirement of steric exclusion with the dihedral angles 8.1° and 96.7° between two pyridyl rings and two phenyl rings, respectively, showing that the 4,4'-oxydibenzoate ligand has more conformational flexibility to sustain the whole crystal lattice. Two Ni(II) centers are bridged via the carboxylate oxygen atoms of the 4,4'-oxydibenzoate ligand, which exhibiting an exo-bidentate coordination mode with the Ni···Ni separation of 14.4705(11) Å and then are further linked by other 4,4'-oxydibenzoate ligands to generate a 1D infinite chain (Fig. 2).

Hydrogen bonding interactions are usually important in the synthesis of a supramolecular network [24]. There are N–H···O hydrogen bonding (N(3)···O(2)^{iii} 2.779(3) Å) and nonclassical C–H···O hydrogen bonding (C(10)···O(1) 2.927(4) Å) (Table 2) interactions

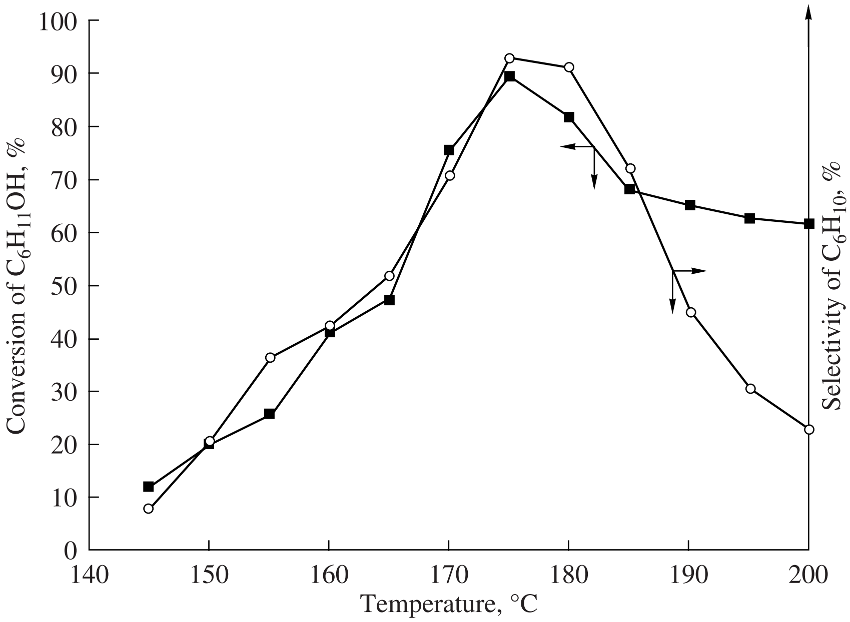

Fig. 4. Catalytic activity as a function of the reaction temperature for complex **I**.

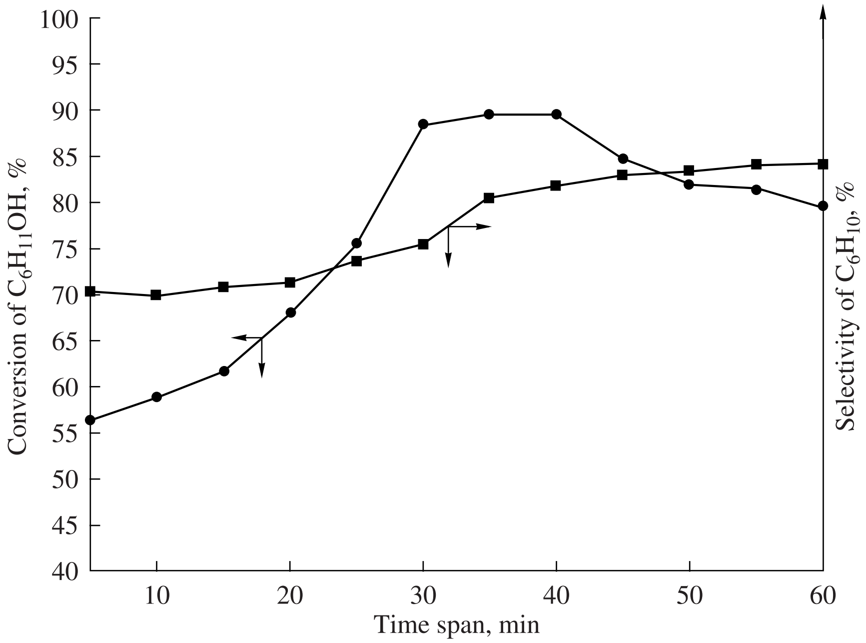

Fig. 5. Catalytic activity as a function of the time span for complex **I**.

between adjacent $[Ni_2(C_{10}H_9N_3)_2(C_{14}H_8O_5)_2]_n$ chains, which indicates that stronger N–H···O and C–H···O hydrogen bonding play an important role in generating a layered hydrogen bonding network. Therefore, through the N–H···O and C–H···O hydrogen bonding interactions, the one-dimensional chains are further linked into a three-dimensional supramolecular network structure (Fig. 3).

The catalytic activity of the title compound **I** for the dehydration of cyclohexanol was studied. The activity and selectivity profiles as a function of the reaction temperature are displayed in Fig. 4. It can be seen that the activity increases monotonously with the increase in temperature during the reaction temperature range 145–175°C, and it decreases rapidly in the temperature region 175–185°C. However, it changes little after 185°C. The result of C_6H_{10} selectivity is similar to the results of catalytic activity during the reaction temperature range 145–185°C. However, after 185°C, the result of C_6H_{10} selectivity still decreases rapidly. Figure 5 summarizes the relationship between the activity and selectivity and the time span at 175°C. It should be pointed out that the activity to $C_6H_{11}OH$ increases monotonously with an increase in the time span before 30 min, and it changes little in the time span of 30–40 min. However, it decreases gradually after 40 min. On the other hand, the C_6H_{10} selectivity increases slightly with an increase in the time span. Hence, the activity and selectivity profiles of the polymer indicate that the optimization temperature and time span are 175°C and 30–40 min for the dehydration of cyclohexanol, respectively.

ACKNOWLEDGMENTS

The work described above was granted by Jinggangshan University and supported by the Education Bureau of Jiangxi, P.R. China (project no. GJJ09339) and the Science and Thechnology Program of Jingganshan University (grand no. JZ0730).

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