ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2011, Vol. 56, No. 12, pp. 1918–1923. © Pleiades Publishing, Ltd., 2011.

A New 3D Supramolecular Array Assembled by Left- and Right-Handed Helical Ni(II) Coordination Polymer Chains Based on 3,5-Dinitrobenzoate and a Flexible Double Imidazole Derivative[1]

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Received July 28, 2010

Abstract—A new nickel(II) coordination polymer with left- and right-handed helical chains [Ni(dmbbbi)(DNBA)$_2$(H$_2$O)] (**1**) has been obtained from hydrothermal reaction of nickel(II) nitrate with a flexible double imidazole derivative 1,1-(1,4-butanediyl)bis(5,6-dimethylbenzimidazole) (dmbbbi) and 3,5-dinitrobenzoic acid (HDNBA). Single-crystal X-ray diffraction analysis reveals that the crystal is triclinic: $a = 9.821(5)$ Å, $b = 13.084(5)$ Å, $c = 14.705(5)$ Å, $\alpha = 105.249(5)°$, $\beta = 95.688(5)°$, $\gamma = 94.273(5)°$, $Z = 2$, $V = 1804.1(13)$ Å^3, $\rho_{calc} = 1.553$ mg/m^3, GOOF = 1.064, the final $R = 0.0360$ and $wR = 0.0999$. The crystal structure analysis indicates that the nickel atom is six coordinated by three oxygen atoms from two DNBA with two kinds of coordination modes, two nitrogen atoms from different dmbbbi and a coordination water molecule forming a [NiN$_2$O$_4$] subunit. The subunits are linked by dmbbbi to form a one dimensional (1D) helical coordination polymer chain and the adjacent chains are further connected by hydrogen bonding interactions to form a novel left- and right-handed helical double-chain structure. The double-chains are ultimately extended into 3D supramolecular structure through π–π stacking interactions. Moreover, thermal stability of title compound and the cyclic voltammetry behavior of compound **1** modified carbon paste electrode (**1**-CPE) in 1 M H$_2$SO$_4$ solution are investigated.

DOI: 10.1134/S0036023611120382

Helical structures, the foundation of the genetic code, have received much attention in coordination chemistry and materials chemistry over the past decade, because helicity is an essential ellement of life and is also important in advanced materials such as biomimetic chemistry and asymmetric catalysis [1, 2]. Many chemists have made great contributions to this field and some single-, double-and multi-stranded helical metal-organic coordination polymer have been obtained by self-assembly processes [3, 4]. However, one of the obvious challenges to chemists is the rational and controllable preparation of the target metal organic compound in this area [5], the formation of which is greatly affected by the ligand nature, counterions and other factors [6–9]. As an important family of multidentate N-donor ligands, double imidazole groups modified aromatic and fatty hydrocarbon as bridging ligand seem to be excellent building block with versatile coordination modes as well as the remarkable coordination ability and stability [10, 11]. On the other hand, noncovalent supramolecular interactions (hydrogen bonds, π–π stacking interactions) as the supramolecular recognition sites may induce the metal-organic coordination polymer to form multistranded helix [4].

On the basis of the aforementioned points, we chose 1,1-(1,4-butanediyl)bis(5,6-dimethylbenzimidazole) (dmbbbi) and 3,5-dinitrobenzoic acid (HDNBA) as the mixed ligands because of their remarkable advantages: (i) Comparing to double imidazole derivative ligands, dmbbbi not only possesses muiti –CH$_2$– groups for freely twisty, but also has the larger aromatic-ring system and may provide potential supramolecular recognition sites for π–π stacking interactions, (ii) As a multifunctional O-donor ligand, DNBA has remarkable coordination ability and many potential H-bonding acceptors to extend the helical structure constructed by dmbbbi ligands and metal cations. Fortunately, a novel nickel(II) coordination polymer with left- and right-handed helical chains [Ni(dmbbbi)(DNBA)$_2$(H$_2$O)] (**1**) has been obtained from hydrothermal reaction and the elemental analysis, IR spectrum, thermal stable and electrochemistry properties of title compound are studied in this report.

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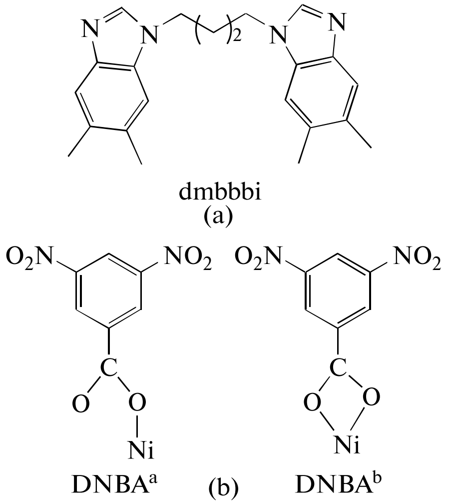

Scheme 1. (a) The N-ligand used in this report; (b) mono-dentate (left) and chelating (right) coordination modes of DNBA.

EXPRIMENTAL

All chemicals purchased were of reagent grade and used without further purification, dmbbbi was synthesized by the method of the literature [12] and characterized by ^{1}H NMR spectrometer analyses and FT-IR spectra. ^{1}H NMR analyses were performed on a Varian Mercury V × 300 spectrometer Analyzer and FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. A CHI 440 Electrochemical Quartz Crystal Microbalance was used for the electrochemical experiments and elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer. Thermogravimetric data for the title compound was collected on a Pyris Diamond thermal analyzer.

Synthesis of [Ni(dmbbbi)(DNBA)$_2$(H$_2$O)] (1). A mixture of $Ni(NO_3)_2 \cdot 4H_2O$ (0.1 mmol), dmbbbi (0.1 mmol), HDNBA (0.2 mmol), NaOH (0.2 mmol), H_2O (10 mL), stirred for 20 min, was sealed to a Teflon-lined stainless steel autoclave (25 mL) and kept at 150°C for 3 days. After the mixture was slowly cooled to room temperature, green block crystals suitable for X-ray diffraction of **1** were isolated by mechanical separation from a green amorphous solid in 42% yield (based on Ni^{II} salt).

For $C_{36}H_{34}N_8NiO_{13}$ anal. calcd. (%): C, 51.14; H, 4.05; N, 13.25.

Found (%): C, 51.18; H, 4.02; N, 13.21.

IR (KBr) (ν, cm^{-1}): 3400 w, 3105 m, 2943 m, 1658 s, 1618 s, 1581 m, 1537 s, 1454 m, 1386 m, 1344 s, 1205 m, 1074 m, 916 m, 727 s.

Preparation of complex 1 modified carbon paste electrode. The modified carbon paste electrode (**1**-CPE) was fabricated as follows: 0.50 g graphite powder and 0.030 g compound **1** were mixed and ground together by agate mortar and pestle for approximately 20 min to achieve an even, dry mixture; to the

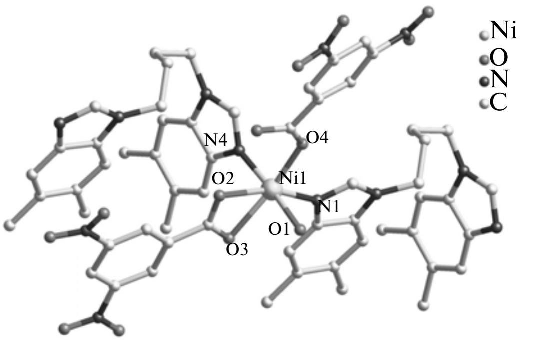

Fig. 1. View of the coordination environment of Ni atom in compound **1**.

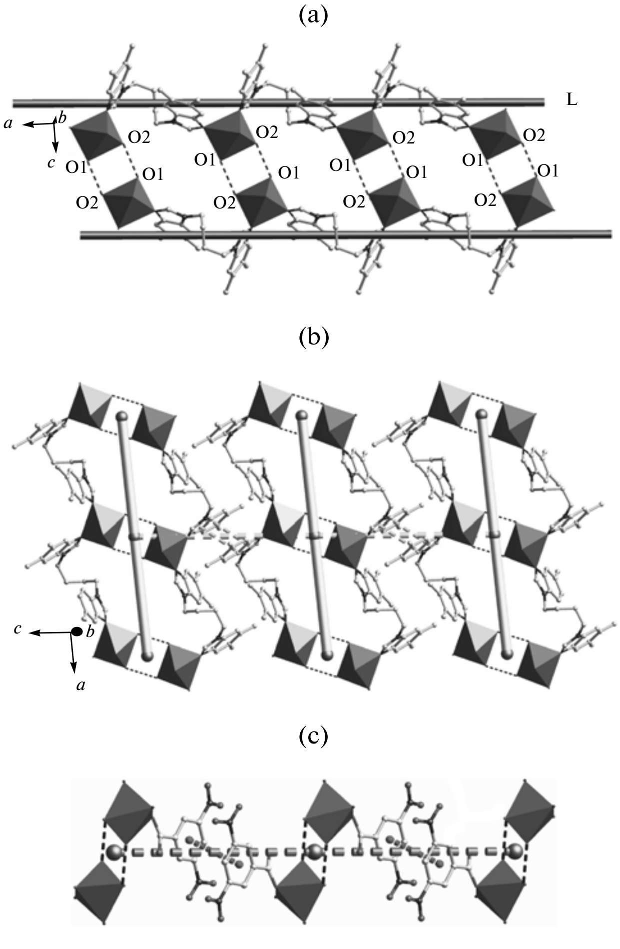

Fig. 2. (a) View of the 1D double-chain structure constructed by single handed helical chains through hydrogen bonding interactions between coordination water molecules (O1) and carboxyl groups (O2) (dotted blue lines), DNBA were omitted for clarity; (b) view of 2D supramolecular network extended by the π–π stacking interactions between the aromatic rings of dmbbbi (dotted sky blue lines); (c) view of the π–π stacking interactions of DNBA^a with a mono-dentate coordination mode (dotted pink lines) in compound **1**.

Table 1. Crystal data and structure refinement for complex **1**

Formula wt.	845.42
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.821(5)
b (Å)	13.084(5)
c (Å)	14.705(5)
α (°)	105.249(5)
β (°)	95.688(5)
γ (°)	94.273(5)
V (Å^3)	1804.1(13)
Z	2
D (g cm^{-3})	1.553
μ (mm^{-1})	0.619
F(000)	872
θ_{max} (deg)	2.45–25.00
Index ranges	$-11 \le h \le 11$
	$-15 \le k \le 15$
	$-17 \le l \le 17$
Reflections collected	14350
Unique reflections	6325
R_{int}	0.0161
R_1^a [$I > 2\sigma(I)$]	0.0360
wR_2^b (all data)	0.0999
GOOF on F^2	1.064
$\Delta\rho_{max}$ (e Å^{-3})	1.047
$\Delta\rho_{min}$ (e Å^{-3})	−0.744

Table 2. Selected bond lengths (d) and bond angles (ω) for complex **1**

Bond	d, Å
Ni(1)–N(1)	2.0641(19)
Ni(1)–O(1)	2.087(2)
Ni(1)–O(2)	2.1185(17)
Ni(1)–O(4)	2.0522(16)
Ni(1)–N(4)#1	2.0989(19)
Ni(1)–O(3)	2.2267(17)
Angle	**ω, deg**
O(4)Ni(1)N(1)	92.75(7)
N(1)Ni(1)O(1)	86.62(8)
N(1)Ni(1)N(4)#1	96.64(7)
O(4)Ni(1)O(2)	104.04(6)
O(1)Ni(1)O(2)	88.80(7)
O(4)Ni(1)O(3)	164.08(6)
O(1)Ni(1)O(3)	86.64(7)
O(4)Ni(1)O(1)	89.04(8)
O(4)Ni(1)N(4)#1	93.32(7)
O(1)Ni(1)N(4)#1	175.87(7)
N(1)Ni(1)O(2)	162.51(7)
N(4)#1Ni(1)O(2)	87.34(7)
N(1)Ni(1)O(3)	102.28(6)
N(4)#1Ni(1)O(3)	90.18(6)
O(2)Ni(1)O(3)	60.58(5)

Note: Symmetry codes: #1 $x - 1, y, z$.

mixture 0.15 mL paraffin oil was added and stirred with a glass rod; then the homogenized mixture was used to pack 3 mm inner diameter glass tubes to a length of 0.7 cm, the surface of the modified CPE was wiped with weighing paper, and the electrical contact was established with the copper stick. The same procedure was used for preparation of bare CPE without Ni complex [13].

X-ray crystallography. A green single crystal with dimensions of 0.22 mm × 0.28 mm × 0.36 mm was selected for X-ray structure analysis. Data were collected on a Bruker Smart Apex II CCD diffractometer with MoK_α ($\lambda = 0.71073$ Å) at 293 K by using an ω–2θ scan mode. 5867 reflections were used in the succeeding refinement. The structures were solved by the direct method and refined by the Full-matrix least-squares on F^2 using the SHELXL-97 software [14, 15]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and the hydrogen atoms of the coordination water molecule were located in successive difference Fourier syntheses. The final $R = 0.0360$ and $wR = 0.0999$ ($w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 1.1179P]$, where $P = (F_o^2 + 2F_c^2)/3$; $S = 1.064$. The crystal data and structure refinement details for **1** are given in Table 1. Selected bond lengths and angles are listed in Table 2. Crystallographic data for the structure reported in this paper has been deposited in the Cambridge Crystallographic Data Center with CCDC reference number 783731.

RESULTS AND DISCUSSION

Single-crystal X-ray analysis shows that compound **1** is a 3D supramolecular network derived from 1D left- and right-handed helical chains extended by hydrogen bond and π-π stacking interactions. The crystal structure analysis indicates that the nickel atom is six coordinated with three oxygen atoms from different DNBA [Ni–O 2.1185(17), 2.2267(17) Å], two nitrogen atoms with a *cis* coordination mode from different dmbbbi [Ni–N 2.0641(19)–2.0989(19) Å] and a oxygen atom from coordination water molecule [Ni–O 2.087(2) Å] showing a octahedral coordination geometry (Fig. 1). The Ni octahedron is slightly distorted, which may be caused by the steric effects of the ligands.

It is worth mentioning that the Ni atoms are linked by dmbbbi to form a 1D helical coordination polymer due to the twisty configuration of the dmbbbi, with a Ni···Ni separation of 9.821 Å and the dihedral angel of the aromatic rings from dmbbbi is 73.08°. Furthermore, the adjacent single handed helical chains are connected by hydrogen bond interactions between the coordination water molecules and chelating carboxylate oxygen atoms to form a interesting left-and right-handed helical double-chain structure [O(1)–H(1A)···O(2), 2.801(3) Å, 160(4)°] (Fig. 2a). The double chains are extended into 2D supramolecular layer through π–π stacking interactions between the aromatic rings of dmbbbi (Fig. 2b). The Cg–Cg (Distance between ring Centroids) distance between benzyl ring and the imidazole ring of dmbbbi ligands from the adjacent double chains is 3.651(2) Å, and the dihedral angels is 1.17°. The adjacent layers are ultimately extended into a 3D supramolecular network by π–π stacking interactions between the aromatic rings of DNBA[a] with the mono-dentate coordination mode [Cg–Cg is 3.653(2) Å, and the dihedral angels is 0°] (Fig. 2c).

To best understand the structure of compound **1**, it is necessary to simplify the building blocks from the 3D supramolecular network. Considering the binuclear Ni cluster linked by hydrogen bonds as a six connected node, the two dmbbbi as the covalent double spacers and the two kinds of supramolecular actions as the non-covalent spacers, the whole structure of **1** can be considered to be a distorted *a*-Po topology network (Figs. 2b, 2c, 3) [16].

To our knowledge, three kinds of interactions are unusually used to link the left- and right-handed helical metal-organic coordination polymer chains, namely: covalence bond, π–π stacking interaction and hydrogen bond. For example, Du and coworkers have obtained a series of double-strand helical chains $[M(pya)_2(H_2O)_2]$ (M = Cu, Co, Ni, pya = 4-pyridylacetic acid) extended by covalence bonds [17]. Chen and coworkers have obtained the first zipper-like double-strand helical chain $[Cu_2(ipa)_2(phen)_2H_2O]$ (ipa = isophthalate, phen = 1,10-phenanthroline) extended by π–π stacking interaction from phen [18]. Hu and our group have prepared two Co(II) metal-organic coordination polymers with left- and right-handed helical chains such as $[Co_2(phen)_2(1,4\text{-}chdc)_2(H_2O)_2]$ (chdc = cyclohexanedicarboxylate) and $[Co(1,3\text{-}BDC)(Dpdq)H_2O] \cdot (H_2O)$ (Dpdq = 2,3-di-2-pyridylquinoxaline) linked by hydrogen bonds [19, 20]. However, most of these helical coordination polymers are derived from the corresponding organic dicarboxylates with the specific coordination angles. The helical character of the title compound is due to the twisty configuration of the dmbbbi and ultimately the 1D chains are extended into double-stranded heli-

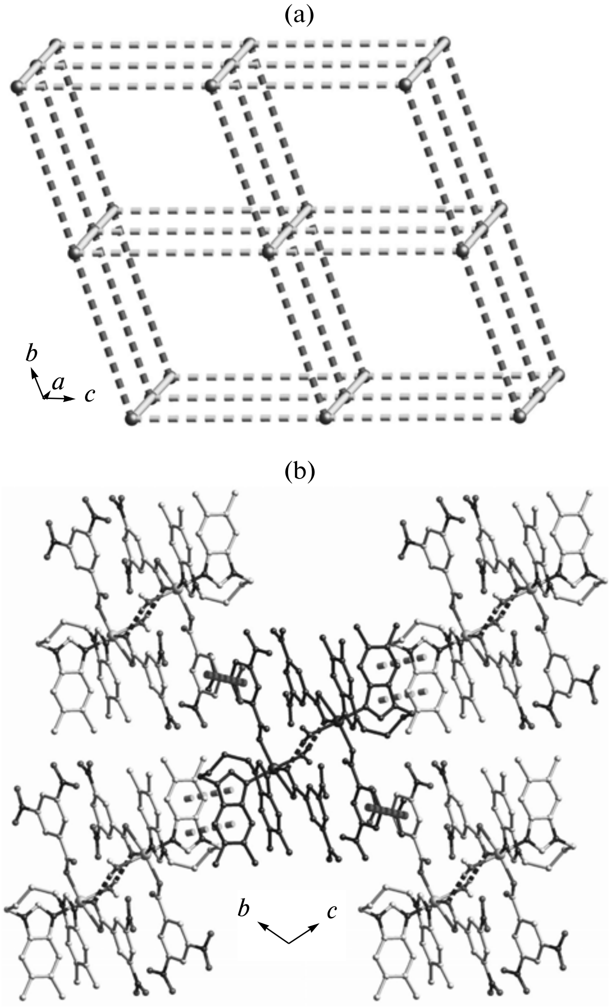

Fig. 3. (a) *a*-Po network of compound **1**; (b) view of the arrangement of the 3D supramolecular network.

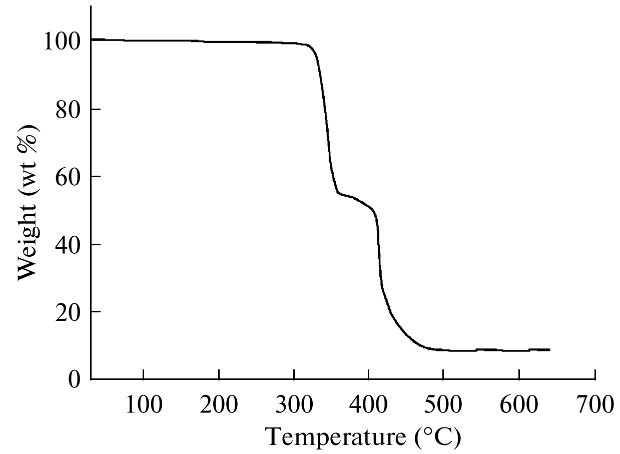

Fig. 4. The TG curve of compound **1**.

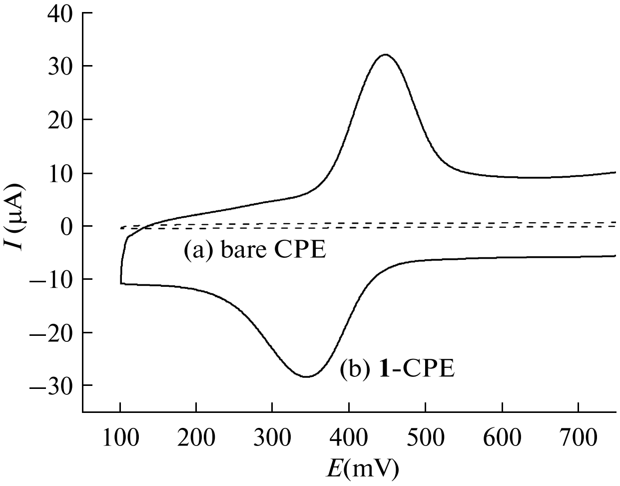

Fig. 5. Cyclic voltammograms of (a) the bare CPE, (b) **1**-CPE in 1 M H_2SO_4 solution in the potential range of 100–750 mV. Scan rate: 100 mVs^{-1}.

cal chains by hydrogen bonds, which is structurally different from that of the reported compounds.

The main features in the IR spectrum of the title compound concern the coordination water molecule, the N-ligands, methyl-, the nitro- and carboxyl groups. The broad band at around 3400 cm^{-1} was assigned to the ν(O–H) vibration of coordinated water molecule [21]. The strong absorption peak at about 727 cm^{-1} and the weak absorptions at about 2943 and 3105 cm^{-1} may be attributed to the ν(C–N) stretching of the imidazol rings and the $-CH_3$ groups of dmbbbi respectively [22], The strong absorption bands at about 1344 and 1537 cm^{-1} arise from the nitro-groups of DNBA [23]. The asymmetric and symmetric vibrations of carboxylate groups appeared at 1658, 1581 and 1386 cm^{-1}, respectively. The Δ values, which represents the separation between ν_{asym}(–COO) and ν_{sym}(–COO), is 272 and 195 cm^{-1}. The Δ values indicate that the carboxylate groups adopt chelating and mono-dentate coordination mode [24].

The TG curve of **1** (Fig. 4) exhibits two continuous weight loss stages in the range of 30–650°C based on the samples consisting of numerous single crystals with a heating rate of 10°C/min. The TG curve indicates that the coordination polymer is stable from room temperature to about 320°C, after which decomposition of the framework occurs. The rapid weight loss corresponds to the loss of the dmbbbi ligand and coordination water molecule. The observed weight loss of 43.13% is in agreement with the calculated one (43.05%). The subsequent weight loss of 50.15% from 360–480°C corresponds to two DNBA ligands and the remaining residue is presumed to be NiO (calcd. 8.83 %; found 8.75%).

Because of the insolubility of compound **1** in water and common organic solvent, the compound **1** bulk-modified carbon paste electrode (**1**-CPE) becomes the optimal choice to study its cyclic voltammetry behavior, which is inexpensive and easy to prepare. Figure 5 shows the cyclic voltammograms at a bare CPE and the **1**-CPE in 1 M H_2SO_4 solution at room temperature. It can be seen from Fig. 5 that in the potential range +100 to +800 mV, there is no redox peak at the bare CPE. While **1**-CPE exhibits one quasi-reversible redox peak and the mean peak potential $E_{1/2} = (E_{pa} + E_{pc})/2$ is approximately 394 mV (100 mVs^{-1}), which could be attributed to the redox of Ni(II)/Ni(I) [25].

A new 3D supramolecular network derived from left- and right-handed helical coordination polymers has been obtained from a flexible double imidazole derivative and 3,5-dinitrobenzoate. The preparation of the title compound demonstrates that the rational design and select of organic ligands is the valid method for the construction of metal-organic coordination polymer with helical structure. Moreover, the compound exhibits the remarkable thermal stability and electrochemistry properties and may be a useful electrochemistry material.

ACKNOWLEDGMENTS

This work was supported by the NCET-09-0853, the National Natural Science Foundation of China (no. 20871022) and the Foundation of Liaoning Province (nos. 2009R03 and 2009A028).

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