

苯二甲酸及咪唑衍生物构筑的一维链状镍配位聚合物的合成、 晶体结构、热稳定性和磁性

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摘要: 以醋酸镍、5-溴间苯二甲酸(H₂BIPA)和 1,4-二咪唑基二甲苯(1,4-bimb)为原料, 在水热条件下合成了 1 个一维链状配位聚合物[Ni(BIPA)(1,4-bimb)(H₂O)₂] (**1**), 利用红外光谱、元素分析、热重、X-粉末衍射以及 X-单晶衍射对其进行了表征。化合物 **1** 是正交晶系, *Pnma* 空间群。该化合物具有一维链状结构, 结构中存在由配位水分子和羧酸氧原子所产生链内氢键作用。详细研究了该化合物的热稳定性和磁性。

关键词: 镍化合物; 晶体结构; 多羧酸配体; 热稳定性

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Synthesis, Crystal Structure, Thermal Stability and Magnetic Property of a One-Dimensional Chain-Like Nickel(II) Coordination Polymer Constructed from the Benzenedicarboxylic Acid and Imidazole Derivatives

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Abstract: A new one-dimensional nickel(II) compound [Ni(BIPA)(1,4-bimb)(H₂O)₂] (**1**) with 5-bromoisophthalic acid (H₂BIPA) and 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bimb) has been prepared by hydrothermal reaction and characterized by single-crystal X-ray diffraction, IR, elemental analysis, TGA and powder X-ray diffraction (PXRD). Compound **1** crystallizes in orthorhombic, space group *Pnma* and features an one-dimensional (1D) chain structure. There exist the intrachain hydrogen bond interactions through the coordinated water molecule and the carboxylate oxygen atoms. Thermal stability and magnetic property of compound **1** were also investigated in detail. CCDC: 811925.

Key words: nickel(II) compound; crystal structure; multicarboxylate ligand; thermal stability

0 Introduction

The rational design and synthesis of coordination polymers are of great interest owing to their variety of

intriguing architectures and topologies and their tremendous potential applications in gas adsorption, catalysis, nonlinear optics, magnetism and luminescence^[1-6]. In this research field, many studies have

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been focused on the suitable organic ligands that can construct new coordination polymers as well as the elucidation of their structure-function relationship^[7-10]. However, it is still a big challenge to prognosticate and explain the relationship because the resulting structures will be determined by many factors, such as the coordination geometry of metal ions, the structural characteristic of ligands, solvent, and so on. In this regard, the selection of suitable organic ligands is extremely important to influence the structures as well as the physical properties. In various organic ligands, carboxylates have been extensively used to prepare coordination polymers due to their various coordination modes. Among the carboxylate ligands, aromatic polycarboxylate compounds have attracted considerable attention in virtue of the robust and versatile coordination capability and geometry of them^[11-15]. However, the aromatic polycarboxylate containing halogen-substituents have received less attention at this stage^[16-19]. 5-Bromoisophthalic acid (H_2BIPA) may be a suitable block to construct novel coordination polymers because of the Br substitutional group. In order to obtain other metal carboxylates with novel structures, an important and useful strategy is to introduce secondary *N*-donor ligands. In this paper, we introduce the flexible bis(imidazole) ligand (1,4-bimb) to the reaction mixture of nickel salt and H_2BIPA under hydrothermal condition. A new mixed ligated nickel carboxylates, namely, $[\text{Ni}(\text{BIPA})(1,4\text{-bimb})(\text{H}_2\text{O})_2]$ (**1**) [1,4-bimb=1,4-bis(imidazol-1-ylmethyl)benzene] is obtained successfully. The single crystal structure, infrared spectrum, thermogravimetric analysis and magnetic property of the compound have been investigated in detail.

1 Experimental

1.1 Materials and methods

All reagents for syntheses and analyses were purchased from commercial sources and used as received without further purification. The bis(imidazole) ligands (1,4-bimb) were synthesized according to the reported procedures^[20]. Elemental analyses were performed using PE 240C Elemental Analyzer. The infrared spectrum of a KBr pellet was

recorded on a VECTOR 22 spectrometer. Thermogravimetric analyses (TGA) were performed with a Perkin Elmer Pyris 1 TGA instrument in the range of 30~800 °C under a nitrogen flow at a heating rate of 10 °C · min⁻¹. Powder X-ray diffraction (XRD) data were collected on a Shimadzu XRD-6000 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=0.154\,056\text{ nm}$). The magnetic susceptibility data of **1** were obtained on a polycrystalline sample using a Quantum Design MPMS-XL7 SQUID magnetometer. The data were corrected for diamagnetic contributions of both the sample holder and the compound obtained from Pascal's constant^[21].

1.2 Synthesis of $[\text{Ni}(\text{BIPA})(1,4\text{-bimb})(\text{H}_2\text{O})_2]$ (**1**)

A mixture of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.025 0 g, 0.1 mmol), H_2BIPA (0.024 5 g, 0.1 mmol), 1,4-bimb (0.024 0 g, 0.1 mmol) and 8 mL of deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at 160 °C for 3 d. After the sample was cooled to room temperature, green block crystals of compound **1** were collected as a pure phase. Elemental analysis calcd. for $\text{C}_{22}\text{H}_{21}\text{BrN}_4\text{NiO}_6$ (%): C, 45.87; H, 3.68; N, 9.73; Found (%): C, 46.02; H, 3.83; N, 10.04. IR (KBr pellet, cm^{-1}): 3 407 (s), 3 136 (m), 1 589 (s), 1 535 (vs), 1 428 (s), 1 358 (s), 1 286 (m), 1 231 (w), 1 123 (m), 1 084 (m), 973 (m), 881 (w), 833 (m), 770 (m), 720 (s), 660 (w), 525 (w).

1.3 Crystallographic studies

Single crystal with dimensions 0.13 mm × 0.10 mm × 0.08 mm for **1** was used for structural determination on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo $K\alpha$ ($\lambda=0.071\,073\text{ nm}$) radiation at room temperature. The data was collected in the θ range 1.93° to 25.99° for **1**, using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s per frame. Numbers of collected and unique reflections are 10 528 and 2 115 ($R_{\text{int}}=0.067\,2$) for **1**, respectively. The data were integrated using the Siemens SAINT program^[22], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full-matrix least

squares using SHELXTL^[23]. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms except those attaching to water molecules were put in calculated positions. The H atoms of water molecules were found from the Fourier maps. All H atoms were refined isotropically with the isotropic vibration

parameters related to the non-hydrogen atoms to which they are bonded. Crystallographic and refinement details of **1** are listed in Table 1. Selected bond lengths and angles are given in Tables 2.

CCDC: 811925.

Table 1 Crystallographic data for compound **1**

Empirical formula	C ₂₂ H ₂₁ BrN ₄ NiO ₆	<i>Z</i>	4
Formula weight	576.02	<i>D_c</i> / (g·cm ⁻³)	1.818
Crystal system	Orthorhombic	<i>F</i> (000)	1 168
Space group	<i>Pnma</i>	Goodness of fit on <i>F</i> ²	1.012
<i>a</i> / nm	1.760 2(3)	<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.037 9, 0.099 6
<i>b</i> / nm	2.105 1(4)	<i>R</i> ₁ , <i>wR</i> ₂ (All data)	0.048 1, 0.101 8
<i>c</i> / nm	0.567 83(10)	Δρ _{max} , Δρ _{min} / (e·nm ⁻³)	667, -530
<i>V</i> / nm ³	2.104 0(7)		

Table 2 Selected bond lengths (nm) and angle (°) for compound **1**

Ni1-N1	0.206 4(3)	Ni1-O1	0.212 1(2)	C5-O2	0.122 3(4)
Ni1-O1W	0.211 7(2)	C5-O1	0.126 2(3)	Br1-C1	0.189 1(4)
N1C-Ni1-N1	180.0	N1-Ni1-O1C	87.00(10)	O1W-Ni1-O1	94.33(8)
N1C-Ni1-O1W	92.23(10)	O1W-Ni1-O1WC	180.0	O1C-Ni1-O1	180.00(6)
N1-Ni1-O1W	87.77(10)	O1W-Ni1-O1C	85.67(8)		

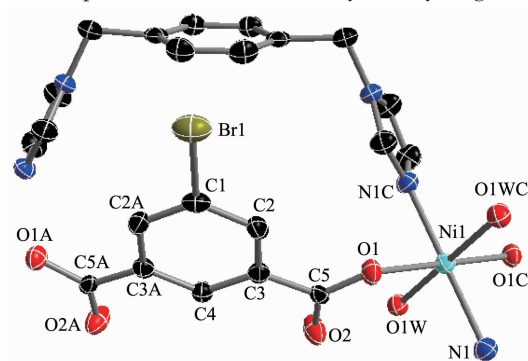
Symmetry transformations used to generate equivalent atoms: A: *x*, -*y*+1/2, *z*; B: *x*, -*y*-1/2, *z*; C: -*x*, -*y*, -*z*+2.

2 Results and discussion

2.1 Description of crystal structure

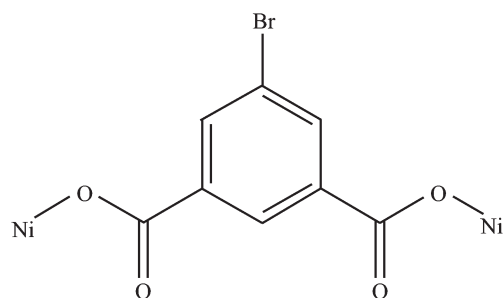
Compound **1** crystallizes in an orthorhombic space group *Pnma*. The asymmetric unit contains a half Ni(II) ion, a half BIPA²⁻, a half 1,4-bimb molecule and one coordination water molecule. Each Ni has a distorted octahedral coordination environment with the six occupied by two carboxylate oxygen atoms (O1, O1C) from two BIPA²⁻, two nitrogen atoms (N1, N1C) from two 1,4-bimb molecules and two coordination molecules (O1W, O1WC) (symmetry code: C: -*x*, -*y*, -*z*+2) (Fig.1). The Ni-O/N bond lengths are in the range of 0.206 5~0.212 2 nm, comparable with those observed in the other Ni-O/N compounds with octahedral environment. In compound **1**, the BIPA²⁻ serves as a bidentate ligand by using two carboxylate oxygen atoms to link two Ni atoms (Scheme 1). The 1,4-bimb molecule bridges the Ni atoms in a *cis*-mode showing an S-shape, and the Ni···Ni distance is 1.052 5 nm through the BIPA²⁻ ligands

to form one-dimensional linear chain structure along the *b* axis (Fig.2, right). There exist the intrachain hydrogen bond interactions (O1W···O1ⁱ 0.2928 nm, symmetry code: *i*: *x*, *y*, *z*+1; O1W···O2 0.256 7 nm). No $\pi \cdots \pi$ interactions are found in the structure. The chains are packed and stabilized by the hydrogen bond



All H atoms except that attached to the water molecule are omitted for clarity; Symmetry code: A: *x*, -*y*+1/2, *z*; B: *x*, -*y*-1/2, *z*; C: -*x*, -*y*, -*z*+2

Fig.1 Coordination environment of the Ni(II) ion in **1** with the thermal ellipsoids drawn at 50% probability level



Scheme 1

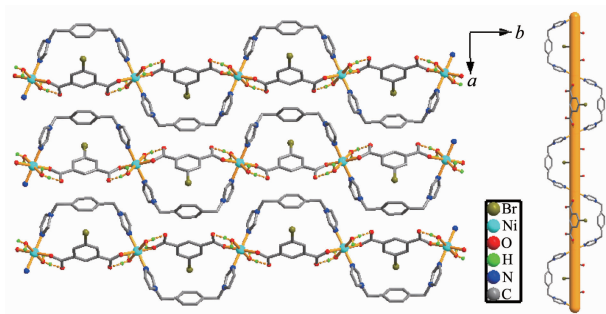


Fig.2 (Left) Structure **1** packed along the *c*-axis;
(Right) 1D chain structure of **1**

interactions to form the one-dimensional chain structure.

2.2 IR spectrum

The IR spectrum of compound **1** shows characteristic bands of the carboxylate stretching vibrations at $1590\sim 1359\text{ cm}^{-1}$ (Fig.3). The absence of the characteristic bands in the range of $1760\sim 1680\text{ cm}^{-1}$ attributed to protonated carboxylate groups in the compound indicates complete deprotonation upon reaction with Ni^{2+} in the compound, in agreement with the single crystal X-ray diffraction analysis^[24], comparable with those observed in the IR spectrum of the H_2BIPA free ligand (1707 cm^{-1}). Furthermore, a series of bands in the $1120\sim 1530\text{ cm}^{-1}$ region associated with the benzi-

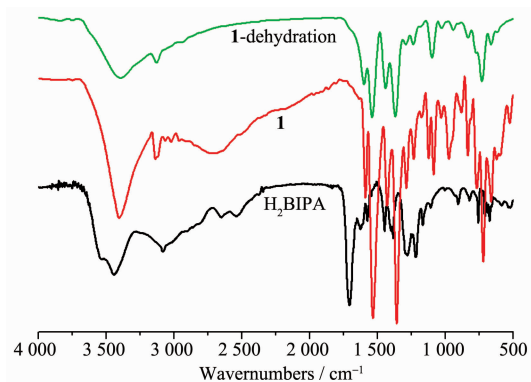


Fig.3 IR spectra for H_2BIPA , compound **1** and compound **1**-dehydrated product

midazole that did not exist in the free ligand.

2.3 PXRD patterns and thermal stability analysis

The simulated and experimental PXRD patterns of compound **1** obtained at room temperature are shown in Fig.5. Their peak positions correspond well with each other, indicating the phase purity of the sample. To characterize the thermal stability of compound **1**, thermal analysis was performed (Fig.4). For compound **1**, the weight loss between 130 and $190\text{ }^\circ\text{C}$ (6.46%) is attributed to the release of one coordination water molecule (calcd. 6.30%). Another plateau is observed in the temperature range $240\sim 290\text{ }^\circ\text{C}$, which may correspond to the release of organic ligands. The residual product keeps stable up to about $360\text{ }^\circ\text{C}$. Between 360 and $400\text{ }^\circ\text{C}$, a quick weight loss of 42.10% is detected. Above 400 up to $800\text{ }^\circ\text{C}$, slowly further weight loss is also observed. XRD measurement reveals that the dehydrated product of compound **1**, which was obtained by heating compound **1** at $200\text{ }^\circ\text{C}$ under a nitrogen flow at a heating rate of $2\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, has different XRD patterns from it for compound **1** (Fig.5).

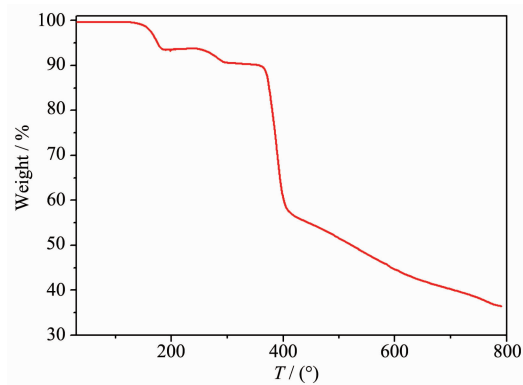


Fig.4 TGA curve for compound **1**

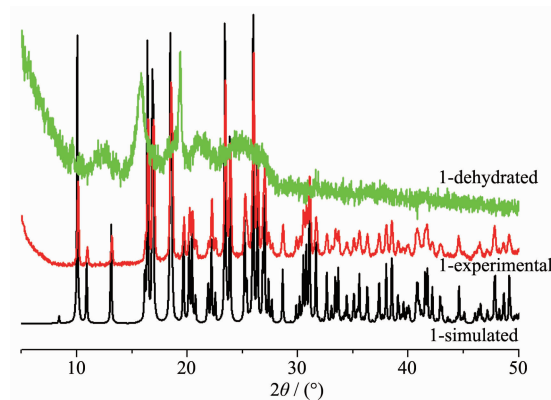


Fig.5 XRD patterns for compound **1** and its dehydrated product

The dehydration process is accompanied by a color change from green to yellow for compound **1**. The color change suggests that, after releasing one coordinated water molecule, the coordinated environment metal ions may be change. The collapse of the structure reveals that the hydrogen bond interactions play an important role in formation of compound **1**.

2.4 Magnetic property

The temperature dependent molar magnetic susceptibilities of compound **1** were measured at 2 kOe in the temperature range 1.8 ~300 K. The room temperature $\chi_M T$ per Ni(II) ion is $1.15 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, close to that expected for the spin-only value of $1.21 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ ($S=1, g=2.2$). In compound **1**, the Ni(II) ions are completely separated by the BIPA²⁻ and 1,4-bimb with the shortest Ni...Ni distance of 1.052 5 nm, the magnetic susceptibility data could be simulated by the theoretical expression for an isolated $S=1$ magnetic spin system considering the ZFS effect (D) based on spin Hamiltonian^[21]:

$$\hat{H}=g\beta H \cdot \hat{S}+D[\hat{S}_z^2-\frac{S(S+1)}{3}]$$
$$\chi_{\text{Ni}}=\frac{2Ng_z^2\beta^2}{3kT}\frac{e^{-\frac{D}{kT}}}{1+2e^{-\frac{D}{kT}}}+\frac{4Ng_x^2\beta^2}{3D}\frac{1-e^{-\frac{D}{kT}}}{1+2e^{-\frac{D}{kT}}}+N_\alpha$$

where N , k and β have their usual meanings and N_α represents the diamagnetic contribution. The best-fitting procedure using the equations gave the set of parameters of $g=2.16$, $D=3.60 \text{ cm}^{-1}$, $N_\alpha=-0.000 51 \text{ cm}^3 \cdot \text{mol}^{-1}$.

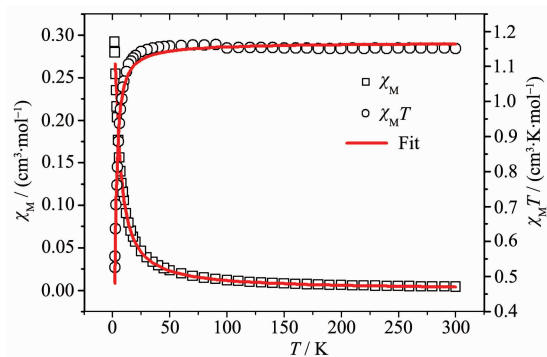


Fig.6 χ_M and $\chi_M T$ vs T plots for compound **1**

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